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TIDAL FLATS IN ESTUARINE WATER QUALITY ANALYSIS

David A. Bella

Oregon State University

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The initial phases of the study involved mixing processes and tidal hydraulics; however, the study emphasis shifted to estuarine benthic systems as the importance of these systems became more apparent. A conceptual model of estuarine benthic systems was developed and a classification system of estuarine benthic deposits which is based on the availability of hydrogen acceptors and reactive iron was developed.

Field studies demonstrated that estuarine sediments and overlying wastes could contain significant concentrations of free sulfides which are toxic to a variety of organisms. Field studies of benthic oxygen uptake and benthic sulfide release were conducted. Water quality profiles within the deposits also were determined. A number of laboratory studies were conducted to determine the rate of sulfate reduction. Results from experiments using extracts from benthic deposits and algal mats demonstrated a close relationship between the rate of sulfate reduction and the sulfate and soluble organic carbon concentrations. A general systems model of estuarine benthic systems was developed. A variety of activities which could contribute to significant environmental changes with estuarine benthic systems were identified.

Methods of determining dispersion coefficients from salinity profiles were examined and an improved method was developed. The build-up of a pollutant in the vicinity of the outfall during the slack water period of tide was studied through a field experiment and mathematical model study.

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TIDAL FLATS IN ESTUARINE WATER QUALITY ANALYSIS

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ABSTRACT

This report summarizes the results of a research project entitled "Tidal Flats and Estuarine Water Quality Analysis." The initial phases of the study involved mixing processes and tidal hydraulics, however, the study emphasis shifted to estuarine benthic systems as the importance of these systems became more apparent. The sulfur cycle was given particular emphasis because:

(1) sulfides, resulting from sulfate reduction within the benthic systems, can influence the benthic oxygen uptake rate,

(2) free sulfides are highly toxic to a variety of organisms, and

(3) the release of hydrogen sulfide may contribute to a deterioration of air quality.

The sulfur cycle is of particular importance in tidal estuaries because of the high sulfate concentrations of saline waters in comparison to fresh waters. A conceptual model of estuarine benthic systems was developed and a classification system of estuarine benthic deposits which is based on the availability of hydrogen acceptors and reactive iron was developed.

Field studies demonstrated that estuarine waters overlying organic rich tidal flat deposits could contain significant concentrations of free sulfides even when dissolved oxygen was present. Field studies of benthic oxygen uptake and benthic sulfide release were conducted. Water quality profiles within the deposits were also determined. A number of laboratory studies were conducted to determine the rate of sulfate reduction. Results from experiments using extracts from benthic deposits and algal mats demonstrated a close relationship between the rate of sulfate reduction and the sulfate and soluble organic carbon concentrations. A general systems model of estuarine benthic systems was developed, however, specific definition of all processes was not possible without further experimental results. A variety of activities which could contribute to significant environmental changes with estuarine benthic systems were identified.

Methods of determining dispersion coefficients from salinity profiles were examined and an improved method was developed. The build-up of a pollutant in the vicinity of the outfall during the slack water period of the tide was studied through a field experiment and mathematical model study.

This report was submitted in fulfillment of Grant 16070 DGO, by Oregon State University in Corvallis under the sponsorship of the Environmental Protection Agency. Work was completed as of November, 1973, with minor revisions made in August, 1974.

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SECTION I

CONCLUSIONS

1. Benthic systems are significant regions of estuarine systems and should not be merely treated as boundary conditions to the overlying waters. The processes occurring within estuarine benthic systems and, in particular, the sulfur cycle, are of major importance with regard to sound environmental management of estuaries. A description of estuarine benthic systems is provided in sections IV and XII.
2. Free sulfide (produced within deposits) can be found at concentrations of approximately 1 mg/L in oxygenated tidal flat waters overlying high organic deposits. Free sulfide concentrations of 50-100 mg/L and higher can be found within the interstitial waters of high organic benthic deposits within several centimeters of the deposit surface. Such concentrations can be toxic to a wide variety of organisms.
3. The presence of high organics within the deposits, available sulfates, low concentrations of available iron, poor drainage, low water velocities and the absence of significant scour are conditions which lead to the build-up of free sulfides within estuarine benthic systems. A variety of human actions can contribute toward these conditions. (See Section XVI)
4. In addition to the conditions described in conclusion 3, low dissolved oxygen concentrations and shallow water depths are conditions which favor higher free sulfide concentrations with the overlying waters.
5. Rates of sulfide production ranging from approximately 10 mg(S)/l-day to 70 mg(S)/l-day were measured by a variety of methods.

6. Rates of sulfate reduction within laboratory experiments using algal extracts were found to be primarily dependent on the sulfate and organic carbon concentrations. The rate of sulfide production in mg(S)/1-day $(\frac{dS}{dt})$ is given by the following equation

$$\frac{dS}{dt} = 77\left(\frac{L^{1.3}}{320 + L^{1.3}}\right)\left(\frac{C}{650 + C}\right)$$

in which L is the sulfate concentration and C is the soluble organic carbon concentration. The rate of soluble organic carbon utilization is given by

$$\frac{dC}{dt} = -0.89\left(\frac{dS}{dt}\right)$$

The rate of sulfate removal is given by

$$\frac{dL}{dt} = -3.1\left(\frac{dS}{dt}\right)$$

7. In situ benthic oxygen uptake rates within tidal flat areas without burrow holes ranged from approximately 1.4 gm/m^2-day to 2.1 gms/m^2-day with the higher rates associated with higher water velocities. Benthic oxygen uptake rates up to approximately 8-9 gms/m^2-day were measured in regions with large numbers of burrow holes. Within such regions, correction of respirometer leakage had to be made.

8. Estimates of benthic sulfide release in tidal flat regions of high organic content were limited and highly variable. These limited results, however,

suggest that benthic sulfide release rates of approximately 1 gm(S)/m^2-day and higher are not unreasonable in tidal flat regions displaying the characteristics described in conclusion 3. It is not now unreasonable to suspect sulfide release from estuarine benthic systems, particularly in tidal flat regions, as a major contributor to atmospheric sulfur.

9. The errors associated with common, finite difference models of advection can be classified into three general categories: (1) oscillation errors; (2) skewness errors; and (3) dispersive errors. The use of the upstream difference method permits correction of these errors.
10. The use of the steady state assumption for measuring longitudinal dispersion coefficients from salinity profiles can lead to a false relationship between fresh water flow and the magnitude of the dispersion coefficients. An improved method of estimating dispersion coefficients from salinity profiles was developed.

SECTION II

RECOMMENDATIONS

1. The magnitude and extent of benthic sulfur release to the atmosphere should be examined on a large scale. It is possible that increases in this release due to a variety of human activities can result in major inputs of atmospheric sulfur.
2. The extent of estuarine benthic deposits containing significant amounts of free sulfide and the influence of human activity on this extent should be examined.
3. A more comprehensive (low level resolution) understanding of the system properties of estuarine ecosystems must be pursued. Only with such an improved understanding can the significance of the more common environmental concerns (e.g. low dissolved oxygen, higher free sulfides, stream flow regulation) be appreciated with regard to the functioning of estuaries within the biosphere. Such studies must place a greater emphasis on the long term consequences of human activities.
4. A more qualitative description of the formation of combined sulfides within benthic deposits should be developed. Such a description would enable a refinement of the systems model presented in section XV. Such a study should proceed at two levels of resolution. The finer resolution would likely deal with the reactions of iron within benthic systems. The lower resolution model should deal with a measurement of the "chemical sulfide demand" (CSD) of a deposit. The CSD would be a measure of the sediment capacity to tie up sulfides in insoluble forms.

5. Studies are needed to quantitatively define the rate of sulfate reduction particularly in the top regions of the anaerobic portions of deposits and immediately below algal mats. Attempts should also be made to develop a measure of the "biochemical sulfate demand" (BSD) of deposited material. The BSD might be a useful concept to incorporate into the lower resolution model of section XV. The ratio, BSD/CSD, would be an indicator of potential sulfide release for a given deposit (generally within the top several centimeters).

6. The concentrations of free sulfides within waters overlying deposits and the amount of hydrogen sulfide released to the atmosphere will depend, in part, on the rate of oxidation of free sulfide. Additional study is needed to better estimate the rate of sulfide oxidation within estuarine waters, particularly at low sulfide concentrations. The age of the water sample should be an important consideration as it appears that recently collected estuarine waters display a more rapid oxidation rate than waters stored for a period of time after collection.

SECTION III

INTRODUCTION

GENERAL BACKGROUND

This is the final report on a three year study entitled "Tidal Flats in Estuarine Water Quality Analysis." This study was supported by the Environmental Protection Agency through Research Grant No. 16020DGO.

GENERAL APPROACH

The technical material presented within this report is generally arranged in logical order rather than in the chronological order that the work was performed in. The writer feels that it would be of value, however, to briefly discuss the general approach used during the study and briefly discuss how this approach often changed the direction of the research.

The general objective of this research is to learn more about estuarine systems and in particular the tidal flat systems, with particular emphasis given to how man's activities can disrupt these systems to the eventual disadvantage of man. The numbers of components and relationships occurring within these systems are so numerous and complex that a complete understanding is essentially impossible. Research effort must be thus directed to study those areas which appear to be of greatest importance. The difficulty is that our knowledge of what we determine to be most important changes as we learn more about the systems. This knowledge (obtained from all sources) hopefully indicates new areas which may be of great importance. A research project must be flexible enough to respond to new information yet stable enough to lead to sound results. Lack of flexibility often results in the pursuit of those items which are already known quite well, while lack of stability can lead to nothing.

In the reported research project, an approach was used in which emphasis was alternately given to mathematical models and experimental results. That is, the experimental results improved the mathematical models while the models in turn suggested where further experimental results might be most profitable. As an example, the oxygen demands of tidal flat areas, particularly the benthal deposits, was recognized from the start as an important consideration. First, laboratory studies were made to study the benthal uptake. Next, a simple mathematical model was developed. From this model, an in situ benthal respirometer was designed, built and run. The results from the in situ benthal oxygen uptake rate studies appeared to be effected by leakage from the respirometer. A mathematical model of the respirometer system was developed and from that model, correction for the leakage was made. The corrected benthal oxygen uptake rates were then studied. The mathematical model results indicated that the experimental results could be best explained if a substantial portion of the measured oxygen uptake rate was due either to the dissolved oxygen, DO, diffusing into the deposits or due to the release of a material which was oxidized rather quickly (half life of several hours or less). Both of these processes suggested that a portion of the benthal uptake (not including benthal plant respiration) might be due to a quickly oxidizing material; the material being oxidized either within the aerobic region of the deposit or within the overlying water. The literature suggested that free sulfides might be such materials. Because free sulfides (particularly hydrogen sulfide) are quite toxic, their presence within the water might often be of greater significance than the low DO values which result, in part, from the oxidation of the free sulfides. It was generally felt at the time, however, that the rapid rate at which free sulfides are oxidized would prevent its presence in waters containing measurable DO. Thus, it was felt, that the free sulfides which were released from the anaerobic regions of the deposit would normally be completely (or near completely) oxidized within the aerobic zone of the deposits. The literature also reflected this notion. A mathematical model of the aerobic zone of the deposits was developed. This model included the downward diffusion of DO, the upward diffusion of free sulfides and the reaction between the two. The model results indicated that under certain conditions, the free sulfide concentrations within overlying waters could be significant. Experimental methods were then developed and significant concentrations of free sulfides were measured in certain areas. Field studies and an exhaustive literature review then led to a qualitative description of what appears at this time to be the important processes leading to both the oxygen uptake and the release of free sulfides. The description of the benthic system exposed important processes for which very little experimental data was available and expansion of the mathematical models without further experimental results would have been unjustified and misleading. Thus the most profitable results during the final phase of the project centered around field and laboratory studies. A general benthic system model was developed, however, it was determined that specific definition of a number of processes required further experimental efforts. The author was reluctant to speculate on certain specific descriptions within the model because such speculation might be too easily accepted without further experimental results.

DETAIL AND PERSPECTIVE

The general research approach followed in this study not only involved a feedback between mathematical model results and experimental results, but also involved a feedback between different views or perspectives of estuarine systems as described below.

The real world appears to be organized into an integrated hiarchy of organizational structures. On an extremely small scale, atoms are organized to form molecules. On a large scale, the planets and sun are organized to form the solar system. Large numbers of intermediate structures, some obvious and some not, are of course present. The definitions of different structures and the disagreements of these definitions will not be pursued. Rather, the point to be made is that a given structure or entity is both made up of components and is also a component of a higher structure.

In order to understand the natural world, man has found it necessary to group what appear to be natural structures into larger groupings. As an example of a functional grouping, individual organisms with similar functions have been grouped into trophic levels. This grouping has enabled man to study the relationships between large groups of organisms. Such a grouping thus enables one to gain perspective, yet because of this larger grouping, one loses detail.

The same real world systems may be studied at a fine level of resolution; (different degrees of grouping). A fine resolution leads to a gain in detail with a sacrifice of perspective while a low resolution leads to a gain in perspective with a sacrifice in detail (precision).

Different investigators (and different professions) often look at the same real world system from different levels of resolution. Such a varied resolution approach often leads to information concerning detail and perspective.*

This project, from the start, has studied the tidal flat system (a loosely defined system having, however, some unique characteristics) from two general views (i.e. at two general levels of organization.) Related component parts which make up the tidal flat system were studied. In addition, the larger estuarine system, of which the tidal flats are components, was also studied.

---

* Author's Note: Some information may require both detail and perspective simultaneously. Such information may well be essentially unattainable. At this time, however, I will not pursue this rather philosophical question of "ecological uncertainty."

Feedback occurred between the results gained from the different views; that is, results gained at one level of organization influenced the direction of work done at the other level of organization. As an example, the dispersion of saline water within an estuary has been a common subject of study. In the early phases of this project, the examination of estuarine dispersion coefficients was pursued. The intrusion of sea water results in conditions withi estuaries which are uniquely different from most fresh water streams. Most mathematical models of estuaries, however, are very similar to those used in fresh water streams with the most common difference being a temporarily varying hydraulic regime. Saline water contains sulfate concentrations many times higher than found in fresh waters (sea water contains 2655 mg/L of sulfates The significance of these higher sulfate concentrations is not apparent until one increases the level of resolution of his view. These higher sulfate concentrations have significant effects upon the benthic systems which, in turn, influence the water quality. One does not appreciate these effects until one views the estuarine bottoms as systems of interacting components and processes rather than boundary conditions to the larger "estuarine systems." Thus, a significant result of the salinity dispersion examined at one level of resolution cannot be appreciated until a finer level of resolution is examined.

THE EVOLUTION OF THE STUDY

The general approach followed in this study can be most simply described as an "evolutionary" process involving feedback between the four general areas illustrated in Fig. 1.

	Math models	Experiment
low level resolution		
high level resolution		

FIG. 1 - AREAS OF FEEDBACK

The study, evolved with the direction of this evolution loosely guided, through the feedbacks, by the three following questions:

1. Is it important?
2. Has it been done or is it being done?
3. Can you do it?

This evolutionary process serves to explain how a project which initially emphasized dispersion coefficients and dissolved oxygen (DO) balance (two popular subjects) shifted to a systems study of the sulfur cycle within estuarine benthic systems (a neglected subject of potentially significant importance).

SECTION IV

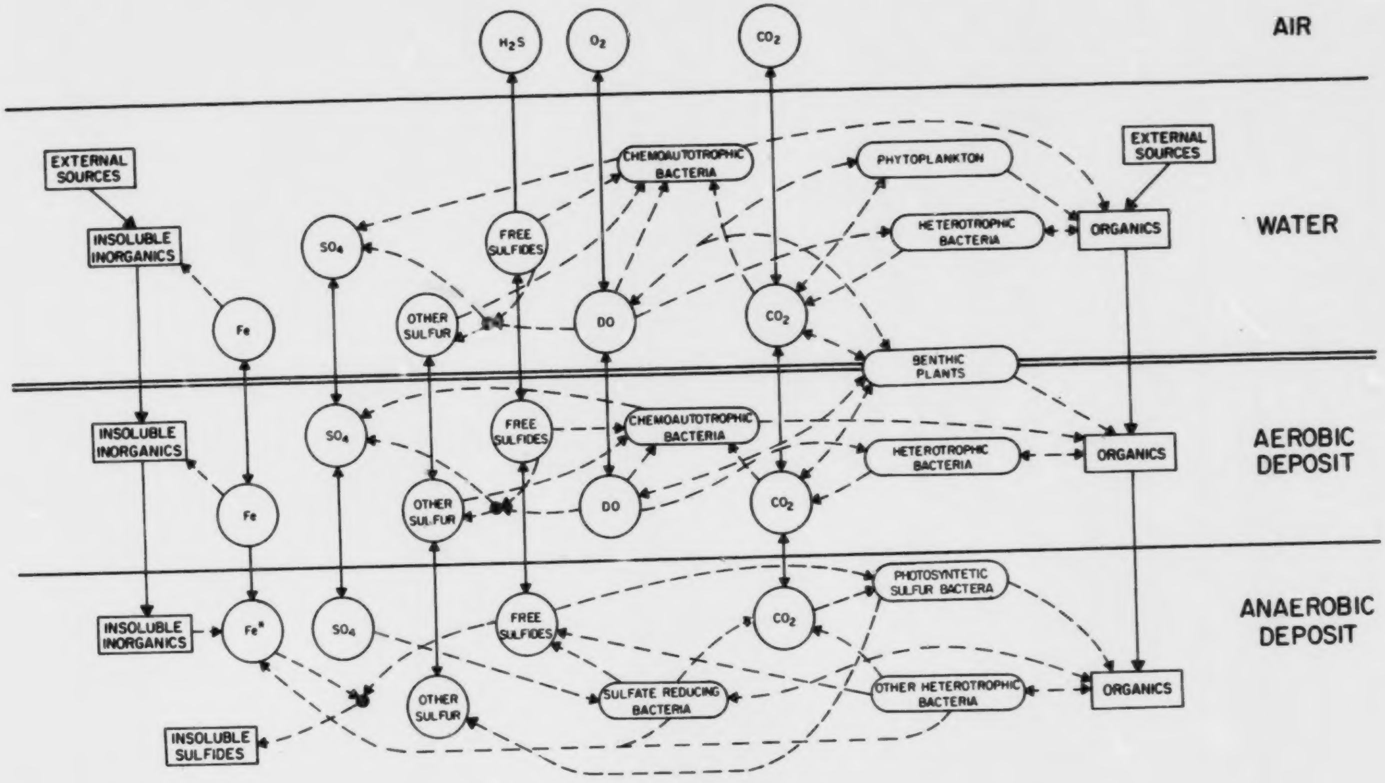
DESCRIPTION OF BENTHIC SYSTEM

INTRODUCTION

The following section will provide a general description of estuarine benthic systems. This description has been developed during the course of this research project through extensive literature searches and field and laboratory investigations (1)(2)(3).

GENERAL BENTHIC SYSTEM

Any approach to an understanding of estuarine benthic systems must involve the complex interactions of the biological, chemical, physical and hydraulic processes. The basis for understanding such systems involves the development of conceptual models. An investigator seeks to develop a simplified model capable of satisfactorily describing certain important aspects of an actual system whose complete complexity is beyond the capacity of the investigator to perceive. In developing a model of a system, one must trade between detail and perspective. Too great a detail makes it difficult to define the relationships between the many components of the model. Sacrifice of detail leads to a better perspective yet eliminates useful information from the model. The level of resolution of the conceptual model presented herein (Fig. 2) was selected to explain certain concepts which are of importance to environmental quality. Omission of certain processes, reactions or other influences should not imply that these omissions are unimportant. Periodic reference to Fig. 2 will help to clarify the following discussion.


AIR
WATER
AEROBIC DEPOSIT
ANAEROBIC DEPOSIT
H_2S
O_2
CO_2
EXTERNAL SOURCES
INSOLUBLE INORGANICS
Fe
SO_4
OTHER SULFUR
FREE SULFIDES
DO
CHEMOAUTOTROPHIC BACTERIA
PHYTOPLANKTON
HETEROTROPHIC BACTERIA
ORGANICS
BENTHIC PLANTS
PHOTOSYNTETIC SULFUR BACTERA
SULFATE REDUCING BACTERIA
OTHER HETEROTROPHIC BACTERIA
Fe^*
INSOLUBLE SULFIDES

SOLID LINES REPRESENT PHYSICAL TRANSFER PROCESS

CHEMICAL REACTION NOTED BY ●

** DENOTES AVAILABLE Fe (also Zn, Sn, Cd, Hg and Cu)*

FIG. 2 - GENERAL BENTHIC SYSTEM

Inorganics and organics are deposited to estuarine benthic systems. Inorganics, including sands, silts and clays, are introduced into estuaries from the ocean, upstream rivers and localized runoff. Organics originate from sources outside the estuary, as well as from primary production within the estuary. The system which results from such deposition is illustrated in Fig. 2.

Decomposition of deposited organics is most often largely microbial with bacteria predominating. (The influence of larger detrital and deposit feeders is discussed in the following subsection.) The type of bacterial decomposition occurring at any location is determined principally by the availability of hydrogen acceptors. When available, dissolved oxygen, DO, is used as the hydrogen acceptor. In its absence, oxidized forms of sulfur, principally sulfate, become the principal hydrogen acceptors. Because nitrate concentrations are nearly always far less than sulfate concentrations within estuarine systems, nitrate reduction, which will occur before sulfate reduction, will not be discussed. The absence of suitable concentrations of both oxygen and oxidized sulfur necessitates the use of endogenous hydrogen acceptors. (For a discussion of endogenous and exogenous hydrogen acceptors see Schroeder and Busch(4)).

The availability of exogenous hydrogen acceptors (DO and sulfates) depends upon the mixing and advection within the deposits. Vertical mixing, and thus the transport of exogenous hydrogen acceptors, is increased by greater water velocities, high concentrations of dissolved oxygen and sulfate within the overlaying water, high permeability of the deposits, and a high rate of turnover by the larger organisms. This latter factor is, in part, dependent on the interstitial water quality. Advection through the deposits depends on the permeability of the deposits and the direction and magnitude of the hydraulic gradient.

The availability of hydrogen acceptors and organics determines the nature and extent of bacterial decomposition which, in turn, largely determines the quality of the interstitial and interfacial waters. The availability of oxygen is an important factor affecting estuarine benthic systems. Oxygen is added to the overlying water by reaeration, photosynthesis and transport due to water movement. The interstitial DO concentration of deposits is determined by a balance between DO transport from above (by mixing and advection) and DO utilization (both chemical and biological) within the deposits.

If the input of organics to deposits exceeds the transfer of DO, aerobic decomposition will not be sufficient to decompose all of the organics. Sulfate reduction will then proceed below the aerobic region. The reduction of sulfates by heterotrophic sulfate reducing bacteria which utilize the sulfate ion as a terminal hydrogen acceptor (5) results in the release of hydrogen sulfide which is found in solution as part of the pH dependent system

$$H_2S \rightleftarrows HS^- \rightleftarrows S^= \qquad (1)$$

In the present discussion, all components of the above relationship will be defined as "free sulfide." At a pH of 6.5-7.0, the free sulfide is approximately evenly divided between H_2S and HS^- with $S^=$ being negligible (6). Free sulfides are also produced during anaerobic putrefication of sulfur containing amino acids, but this process is felt to be of lesser importance in the marine environment (7,8).

Free sulfides form insoluble compounds with heavy metals, particularly iron. Free sulfide quickly reacts with available iron within the deposits to form ferrous sulfide, FeS, which gives benthic deposits their characteristic black color (9). The input of this iron into the deposits results primarily from the deposition of insoluble inorganics, which contain ferric oxides and other insoluble forms of iron. Not all of this iron, however, is available to react with the sulfides. Some additional reactive iron originates from the decomposed organics. This latter source is usually less and thus the supply of available iron within the deposits is often largely dependent on the nature and extent of inorganic deposition (10). Other heavy metals such as zinc, tin, cadmium, lead, copper and mercury all have solubility products significantly below that of ferrous sulfide and thus, the presence of ferrous sulfide indicates that ionic solutions of these metals within the interstitial waters are not likely to be significant.

Free sulfide concentrations within benthic deposits will remain at low levels (generally below 1 mg/l) when available iron is present. If available iron is sufficiently depleted, free sulfides within the anaerobic regions of deposits will increase until their production at a given location is balanced by the advective and diffusive transport out of that location and by the loss caused by reaction with any remaining available iron. Measured free sulfide concentrations up to approximately 130 mg/l were found within interstitial waters of tidal flat deposits though some loss may have occurred during the analysis. Theoretical investigations indicate that maximum concentrations might be several times higher if all available iron is depleted.

If the aerobic layer of the sediment is thin enough to allow light to penetrate to the anaerobic zone, populations of photosynthetic purple and green sulfur bacteria may develop, utilizing the free sulfides as hydrogen donors, and producing free sulfur as a by-product. This may occur below an algal mat and is possibly due to the lower compensation point for bacterial photoreduction, and to the ability of the photosynthetic bacteria to utilize longer wavelengths of light than can the algae (8,11).

If the rate of free sulfide production exceeds the rate at which it can be converted to nondiffusible forms, such as ferrous sulfide or insoluble free sulfur, the sulfide may diffuse upward into the aerobic regions of the sediment or into the water column. Here it will be oxidized to sulfite, thiosulfate, sulfate, or free sulfur (7,12,13).

The chemical reaction of free sulfides in aqueous solutions has been studied by many investigators (7,12,13,14,15,16). Half lives of free sulfide, in aqueous solutions, ranging from 15 minutes to 70 hours have been reported. Several studies have described the oxidation of free sulfides to occur via second order kinetics (6,7,12); however, such a description is a simplification of an extremely complex chemical temperature, pH, and initial oxygen and sulfide concentrations are all factors affecting the rate of oxidation (7,12). The oxidation of free sulfide is catalyzed by the presence of metallic ions, such as of Ni, Mn, Fe, Ca, and Mg, and is accelerated by some organic substances such as formaldehyde, phenols, and urea. Thus, the oxidation of free sulfides in estuarine and marine water may be much more rapid than in distilled water due to the presence of catalysts. Within oxygenated sea water the half life of sulfide has been reported to vary from 10 minutes to several hours (7,13,17). Studies indicate that estuarine waters stored for a period of time after collection will display slower oxidation rates of free sulfides than freshly collected waters (18). Since HS^- predominates at the pH of sea water, it has been proposed that the oxidation proceeds by the following reaction (19).

$$2HS^- + 2O_2 \rightarrow S_2O_3^{=} + H_2O \qquad (2)$$

Following the above chemical oxidation, the thiosulfate ion is more slowly oxidized to sulfate, probably with the intermediate production of other oxidized forms. Sulfur oxidizing bacteria of the genus Thiobacillus appear to be important in this final oxidation step (20,21).

If the benthic deposits are overturned or flushed with oxygenated water, ferrous sulfide will be rapidly oxidized. Overturned sediments will normally return to anaerobic conditions. A portion of the ferrous sulfide iron will be returned to the sediment as available iron which can further react with free sulfide to form more ferrous sulfide. Thus overturning and flushing of sediment with oxygenated waters results in a recycling of available iron.

When oxidation of sulfides occurs, either inorganically or by sulfur oxidizing bacteria, some of the free sulfide and ferrous sulfide is oxidized to elemental sulfur. In an anaerobic environment elemental sulfur then slowly reacts with FeS to form pyrite. This latter reaction occurs on a time scale of years and may lead to a more permanent depletion of available iron.

Free sulfide can be released to the overlying water even if these waters do contain DO. Experimental and theoretical results presented in a latter section of this report demonstrate that free sulfide concentrations of approximately 1 mg/l can persist in shallow tidal flat open waters as a result of benthic sulfide release even when the DO of these waters is in the 4-6 mg/l range. Hydrogen sulfide may also be released to the atmosphere particularly when the water depths are shallow or the benthic systems are exposed.

High concentrations of free sulfides within the deposits and the release of free sulfides to the overlying water and atmosphere can be environmentally significant for a number of reasons; among these are the following.

1. The release of free sulfides can increase the benthic oxygen demand rate and thus lead to a decline in the aerobic zone of the deposit and a lowering of the DO concentrations within the overlying waters, particularly with the interfacial regions. Though these interfacial regions constitute a very small fraction of the estuarine water mass, they are of high ecological importance.
2. Free sulfides, particularly hydrogen sulfide, are toxic at low concentrations to fish, crustaceans, polychetes and a variety of benthic microinvertebrates (8,16,20,22,23,24). Actual toxic concentrations may be considerably lower than some reported in the literature because of initial sulfide concentrations within batch tests are often reported. Average concentrations throughout the test period may be considerably lower due to chemical oxidation. In tests which maintained nearly constant conditions, hydrogen sulfide concentrations below 0.075 mg/l (pH 7.6-8.0) were found to be significantly harmful to rainbow trout, sucker, and walleye, particularly to the eggs and fry of these fish (22).
3. The release of hydrogen sulfide to the atmosphere can cause an air pollution problem. Not only does hydrogen sulfide have an

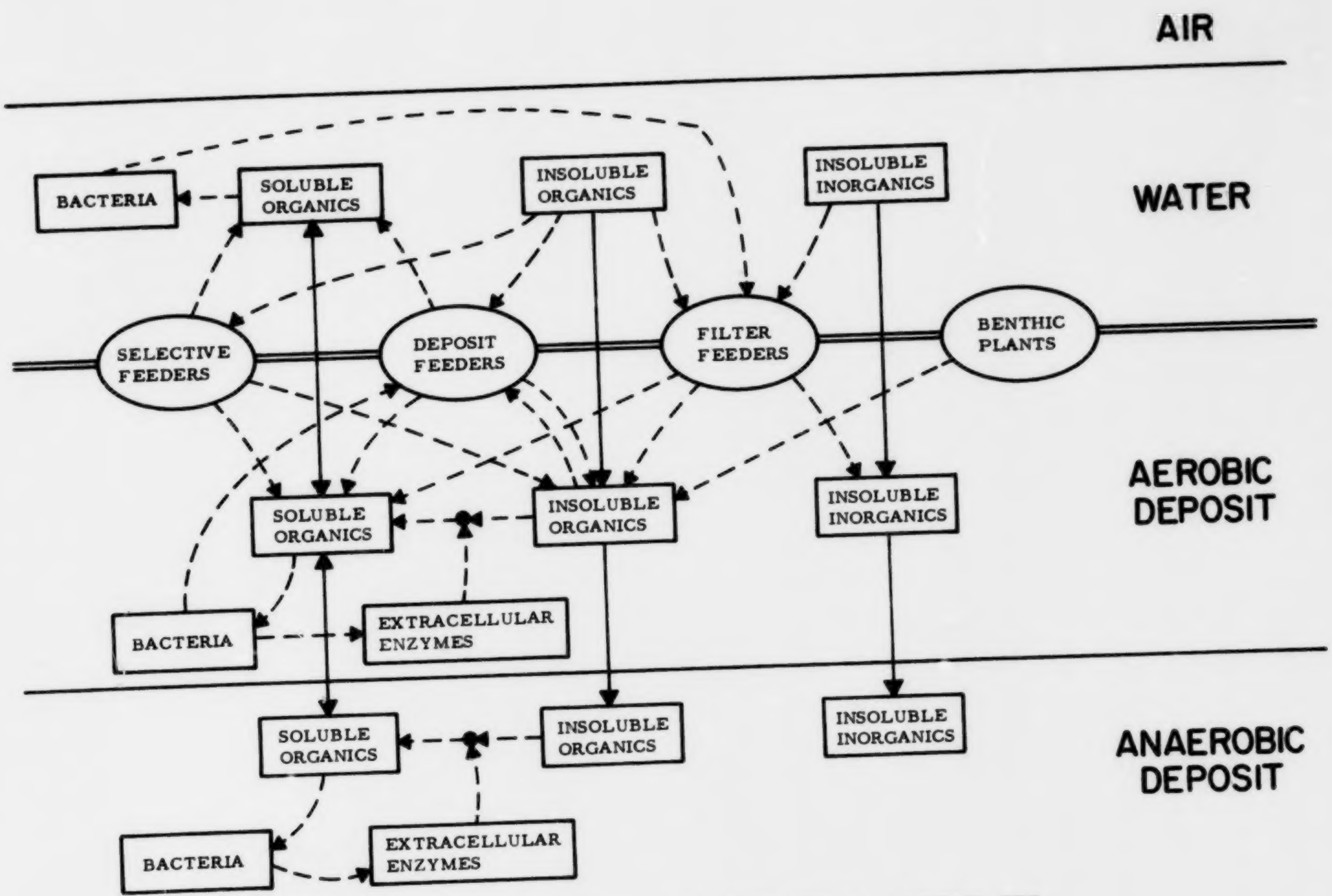
undesirable odor but it is also toxic. Moreover, the release of hydrogen sulfide from tidal flat areas may be a significant input of atmospheric sulfur (25)(26)(27).

If the solubilization of organics at a given depth exceeds the downward transport of DO and sulfates to that depth, decomposition of organics below this depth must proceed through the use of endogenous hydrogen acceptors (not shown in Fig. 2). Increased accumulation of organics can be expected, particularly if the absence of available iron results in free sulfide concentrations sufficiently high to inhibit endogenous decomposition. Methane fermentation will occur below the region of sulfate reduction if conditions are suitable. Formation of gases (principally methane) within these regions may lead to the disruption of the bottom, and the release of free sulfides to the overlying water.

LARGER PLANTS AND ANIMALS

The animal component of estuarine benthic ecosystems can be generally divided into infauna (animals that live within the sediments) and epifauna (animals that live on the sediment surface or just above it). Some infauna make ephemeral pockets in the sediment which are filled as the animal moves on; others make more permanent burrows and bring overlying water into the sediment. Much of the infauna is microscopic, living among the sediment particles.

Although the separation of benthic animals into infauna and epifauna can be useful, the following discussion will rely more on feeding behaviors(2). Benthic animals are divided into three feeding types: selective particle feeders, deposit feeders and filter feeders. (see Fig. 3)


AIR
WATER
AEROBIC DEPOSIT
ANAEROBIC DEPOSIT
BACTERIA
SOLUBLE ORGANICS
INSOLUBLE ORGANICS
INSOLUBLE INORGANICS
SELECTIVE FEEDERS
DEPOSIT FEEDERS
FILTER FEEDERS
BENTHIC PLANTS
SOLUBLE ORGANICS
INSOLUBLE ORGANICS
INSOLUBLE INORGANICS
BACTERIA
EXTRACELLULAR ENZYMES
SOLUBLE ORGANICS
INSOLUBLE ORGANICS
INSOLUBLE INORGANICS
BACTERIA
EXTRACELLULAR ENZYMES

INSOLUBLE ORGANICS WITHIN WATER INCLUDE PHYTOPLANKTON, ZOOPLANKTON, DETRITUS, ETC.

FIG. 3 - CONCEPTUAL MODEL OF LARGER ANIMALS WITHIN BENTHIC SYSTEM

Selective particle feeders may be herbivores, predators, or scavengers. They may feed on whole organisms which they actively capture, or they may feed on fragments of plants or animals. Crabs, some worms, most fishes, and other more mobile species fall into this category. The food contains little inorganic material and is generally broken down by mechanical processes and then by chemical processes. The residues, inorganic materials, undigestible organics, and resistant bacteria, are combined with mucous and coated to form distinctive fecal pellets. Fecal pellets generally settle to the bottom and may make up from 30% to 50% of the sediment, and in extreme cases, where quiet bottom waters occur, they may account for up to 100% of the sediment (28)(29). The fecal pellets of carnivores are generally loose pellets those of herbivores harder, and those of deposit feeders hardest. Many of the pellets have characteristic shapes, size, and sculpturing, and are of taxonomic importance. Some are quite fragile while others may persist for more than 100 years.

There are two general types of deposit feeders. Some move through the sediment and take in the sediment as they go, digesting what they can of the organic material and discarding as feces the undigestible organics and the inorganic residues. These animals are mostly worms in estuaries and are not generally in direct contact with the waters which overly the sediments. Other deposit feeders bury themselves in the sediment but have siphons or other extensions through which they "suck up" detritus that has recently fallen to the sediment surface. Certain clams and worms feed in this way. Again these species feed unselectively on the available food and are usually unable to sort food very efficiently. Food of deposit feeders is broken down chemically, and in some cases mechanically, and the residues are formed into fecal pellets which contain much greater quantities of inorganic materials than do feces of other feeding types.

Filter feeders sieve water and remove particulate material. Mussels, some clams, and some worms are examples of this category. Most filter feeders use cilia to create currents of water over a mucous network which entangles particles. These are called ciliary mucous feeders. Mussels are good examples. Other species, particularly tube dwellers, may force water through the tube with peristaltic body movements. *Urechis caupo*, the sausage worm, is an example. The particle laden mucous is then taken into the digestive system. Some clams "sort" the particles before they are taken into the digestive system and discard the unusable sizes in mucous masses as pseudofeces. The food that passes through the digestive tract does not usually require mechanical maceration and is digested chemically. The feces of filter feeders are primarily organic.

Not all animals fit neatly into these feeding categories. Some deposit feeders may be somewhat selective, and some selective feeders may be quite nonselective if food is scarce. Some animals like starfish that utilize extra-corporeal digestion are true predators but do not otherwise fit neatly into the selective feeding type.

Animals tend to break down larger particles through maceration and digestion. The formation of fecal pellets places these particles on the bottom rather than returning them to the water to increase the turbidity. The fecal pellets are finally degraded by bacteria, but may pass through several deposit feeders before final mineralization.

Certain animals, particularly ciliary-mucous feeders have a marked effect on the turbidity of the overlying water (30). These organisms remove particulate matter from the water and compact much of it in the form of pseudofeces which are larger than the suspended particles and therefore sink more rapidly to the bottom. This reduction in turbidity permits more light to reach the benthic algae, enhancing the photosynthetic process and increasing the daylight DO. At the same time, the removal of CO_2 tends to raise the pH during the daylight hours. Soluble organic wastes of all feeding types are discarded into the water or interstitial water depending on the habitat of the particular species.

Some benthic plants also tend to stabilize the benthic environment. Algal mats can serve to reduce erosion of benthic deposits. When such mats become extensive, they can significantly contribute to the formation of free sulfide in the deposits below. Other plants, such as eelgrass, send roots into the sediment, and many burrowing animals construct tubes that also reduce erosion. These roots and tubes also provide shelter for infaunal species and may contribute to their food as well.

Animals also influence vertical mixing within the sediment. There is a great deal of mechanical mixing as burrowing species construct their tubes or move through the sediment. Fecal pellets of infaunal species are frequently brought to the surface and deposited there. Burrows may extend more than a meter into the sediment and the constant reworking of sediment insures a relative homogeneity of the sediment to that depth. Burrows also provide a route for oxygen to reach into the sediment, and although sediments may be anaerobic a few millimeters beneath the surface, there will usually be an aerobic region immediately surrounding each burrow if the overlying water is not devoid of oxygen. Conversely, burrows serve as a route through which waste materials such as fecal pellets and dissolved organics can move out of the sediment. Burrowing activities also serve to release inorganic nutrients to the surface water where they may be utilized by photosynthetic plants. Wave action over a beach filled with tubes may cause a pumping action through the tubes, increasing aeration and, possibly, erosion of the wall of the tubes. Such mixing can also contribute to the oxidation of combined sulfide (such as FeS) and the "recycling" of iron to combine with produced sulfide and thus prevent high levels of free sulfide.

The major role of green plants is to convert solar energy into a form that can be used by plants and animals. Through the photosynthetic process inorganic substances are converted into high-energy organic compounds. This primary production is the ultimate source of food for all organisms. Phytoplankton, benthic algae and eelgrass are all important primary producers within estuarine ecosystems. Organic materials produced by the plant components are transferred through herbivores and several levels of carnivores to the sediments. Feedback occurs frequently so that the web concept is more descriptive than the food chain. In the sediment, these materials are mineralized to their inorganic end-products and then may again enter the cycle.

The role of particles in the marine water often is not appreciated. Heavy metals may adsorb to these particles and if the particles remain in suspension they may be carried far to sea before they settle. These metal-laden particles may, however, be pelletized by various animals and deposited. The role of animals in removing such particles may be very important.

Many of the effects that have been discussed deal with the transportation of materials from the water to the sediment, but there is transport in the other direction as well. Benthic species almost always have pelagic larvae. Essentially all of these larvae must feed and develop within open water regions, returning to the sediment for later life stages. Pelagic stages thus insure wide dispersal of these species. Propagation of benthic animals thus depends on the ability of pelagic life stages to leave the sediment.

SECTION V

DESCRIPTION OF SITES USED FOR FIELD STUDIES

Five sites were used during various stages of this study for the field studies. The four sites located within Yaquina Estuary are shown in Fig. 4. Site 1 was located on the south side of the estuary immediately to the east of the Oregon State University Marine Science Center. This site lay within approximately one mile of the estuary mouth, and was strongly influenced by marine water. High salinities (33-35 parts per thousand), low temperatures (45-50°F), and high tidal current velocities (0.6 - 0.8 feet per second) were characteristic here. This area appeared to be fairly remote from any major source of industrial pollution, and no excessive domestic contamination was evident. The sediments here were heavily colonized between +4 and +6 feet above mean low low water (MLLW) by large populations of the mud shrimps *Callinassa californiensis* and *Upogebia pugettensis*. They were very active in burrowing and mixing of the sediments at this elevation. There was a distinct lack of attached vegetation in this range, but summer growth of the benthic alga *Enteromorpha* and of *Zostera* was extensive below +4 feet MLLW. At approximately +7 feet MLLW the sediment was covered by a thin, but very firm mat of unidentified algae. A transect of total sulfides, redox potential and volatile solids at site 1 is shown in Fig. 5.

Site 2 is located in the eastern portion of the Sally's Bend area of Yaquina Bay. Water velocities were high at times though usually slightly lower than site 1. Burrowing by benthic invertebrates was common in this region. During summer periods, benthic algal growths were noticeable. Only limited studies were conducted at this site.

Site 3 is approximately three miles upstream of site 1 on the east side of the Yaquina estuary adjacent to Parker Slough. Waters here are slightly less saline, have higher temperatures, and slightly lower tidal velocities compared to site 2. Burrowing by benthic invertebrates is extensive, as are mid-summer blooms of the benthic alga, *Enteromorpha*. The only studies conducted at this site were measurements of benthic oxygen uptake rates.

Site 4 was located about 14 miles upstream and 300 feet east of the Yaquina River bridge at Toledo. Unlike site 1, this site lays in an industrialized area characterized by extensive log rafting and wood processing operations. The effect of fresh water was reflected in the lower summer salinities (14-20 parts per thousand). Water temperature was higher than at site 1, current velocities still fairly high, and the sediments were often covered by large quantities of bark chips. Burrowing organisms and dense growths of benthic algae were lacking.

Site 5 was located on the south side of Isthmus Slough in the Coos Estuary. This site was located on a mud flat which was relatively protected from the main channel currents by a dike and log storage area. Tidal velocities were low, temperatures comparable to those at site 2, and salinities intermediate between those of sites 1 and 2 (28-30 parts per thousand during summer months). A number of sulfite process woodpulping mills were located nearby. Extensive algal mats primarily of a salt water species of *Vaucheria* were characteristic here, but burrowing organisms were not evident. Organic content of the sediments was high. A general purplish coloration to the water was very noticeable due to the photosynthetic purple sulfur bacteria.

A comparison of particle size for the three major sites is given in Table 1. Bacterial counts for sites 1, 2, 4 and 5 are given in Table 2.

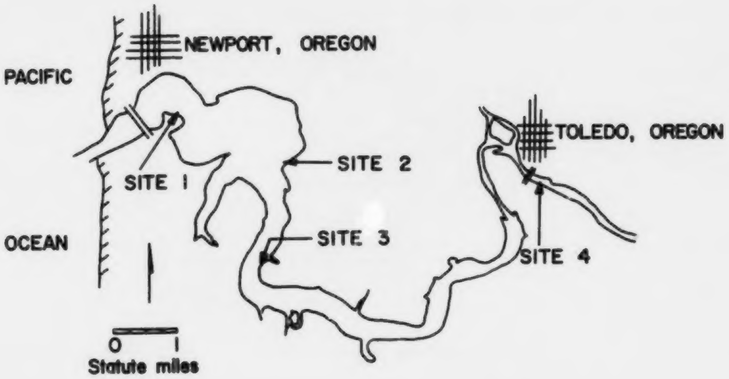

NEWPORT, OREGON
PACIFIC
TOLEDO, OREGON
SITE 2
SITE 1
SITE 3
OCEAN
SITE 4
0 1
Statute miles

FIG. 4 - SITES LOCATED ON YAQUINA ESTUARY

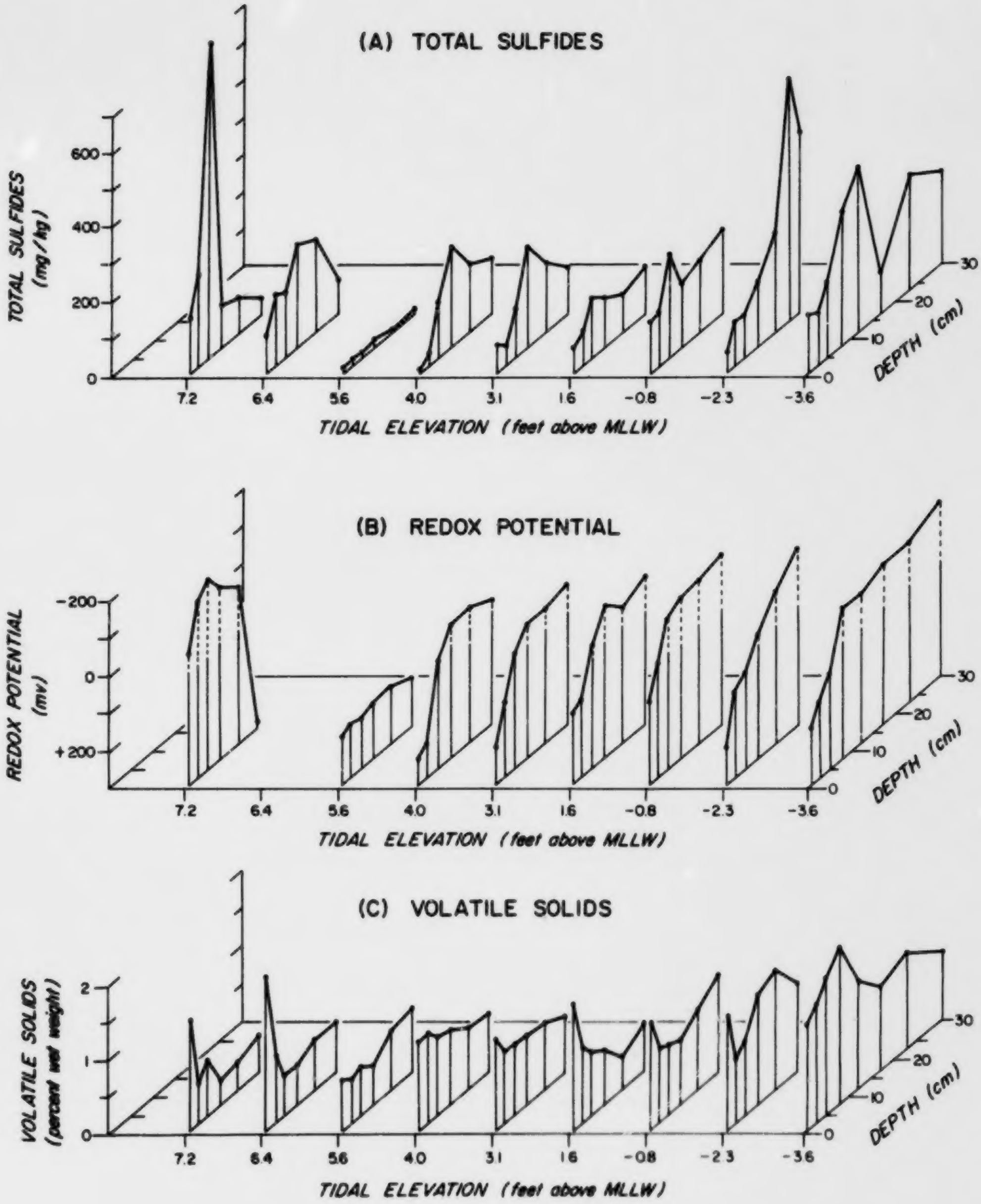


FIG. 5 - TRANSECT AT SITE 1 - SUMMER 1970

TABLE 1. PARTICLE SIZE FOR SAMPLING SITES

	Site 1		Site 2		Site 3	
Depth (cm)	Sand (a)	Silt and clay (b)	Sand	Silt and clay	Sand	Silt and clay
0 - 1	92.2	7.8	15.8	84.2	2.9	97.1
2 - 3	99.3	0.7	14.0	86.0	1.3	98.7
4 - 5	87.6	12.4	8.0	92.0	0.6	99.4
7 - 8	93.1	6.9	9.7	90.3	2.3	97.7
11 - 12	95.3	4.7	11.9	88.1	3.9	96.1

(a) Percent of particles larger than 63 microns.
(b) Percent of particles smaller than 63 microns.

TABLE 2. BACTERIAL COUNTS PER GRAM OF WET SEDIMENT (SUMMER, 1970)

Location	Depth	Total Plate Count(a)	Sulfate Reducing Bacteria(b)
Site 1, 3.1 ft. MLLW	0- 1 cm(c)	6.3×10^6	3.6×10^2
	2- 3 cm(c)	4.7×10^5	7.3×10^2
	4- 5 cm(c)	1.5×10^5	3.6×10^2
	10-11 cm(c)	4.5×10^4	300
Site 1,-2.3 ft. MLLW	0- 1 cm(c)	5.5×10^6	4.8×10^3
	2- 3 cm(c)	1.2×10^6	4.2×10^3
	4- 5 cm(c)	1.2×10^6	5.7×10^3
Site 2	0- 1 cm(c)	6.5×10^6	4.7×10^4
	10-11 cm(d)	3.5×10^5	1.3×10^4
	20-21 cm(d)	4.2×10^5	1.7×10^3
	27-28 cm(d)	1.1×10^5	1.3×10^3
	30-31 cm(d)	1.2×10^5	1.8×10^3
	35-36 cm(c)	4.4×10^4	2.8×10^2
Site 4	0- 1 cm(f)	3.7×10^6	1.2×10^5
	10-11 cm(f)	2.9×10^5	6.7×10^3
	20-21 cm(f)	1.9×10^5	4.2×10^3
	30-31 cm(e)	2.6×10^5	8.8×10^3
Site 5	0- 1 cm(c)	1.4×10^7	2.5×10^5
	2- 3 cm(c)	2.5×10^6	3.4×10^4
	4- 5 cm(c)	1.4×10^6	4.6×10^4
	7- 8 cm(c)	7.9×10^5	8.4×10^3
	11-12 cm(c)	2.2×10^5	6.8×10^3

(a) On marine agar 2216 (numbers per gram of wet sediment)
(b) MPN using modified SIM medium or a modified medium for halophilic sulfate reducing bacteria (30). (numbers per gram of wet sediment)
(c) Determined on 1 date
(d) Average on 2 dates
(e) Average on 3 dates
(f) Average on 4 dates

SECTION VI

STUDIES OF BENTHAL OXYGEN UPTAKE

INITIAL LABORATORY STUDIES

During the early stages of this project, a series of laboratory tests were conducted to determine the oxygen uptake rate of deposits removed from site 4 (32)(33). Mud cores were obtained by inserting 3-inch plastic tubes into the deposit. The tubes, with the deposit, were removed to the laboratory where tests were conducted within the same tubes to determine the benthal oxygen uptake. Mixing within the overlying water was provided by a plunger type mixing device.

These early laboratory results determined a benthic oxygen uptake rate of approximately 1.9 gm/m^2/-day under conditions of low mixing and an uptake rate of approximately 3.4 gm/m^2-day under conditions of higher mixing. It was found that the depth of the deposits had no effect on the oxygen uptake rate between the depths of 5.1 and 30.5 cm. When $HgCl_2$ was added to the water the DO uptake rate decreased to one third of its value at both the lower and higher mixing ranges. These early laboratory studies provided information for the design of the field respirometer described below.

EXPERIMENTAL DESIGN AND PROCEDURE FOR FIELD STUDIES

Light and dark benthal respirometers developed during this research were constructed from plexiglas half cylinders, 5.64 meters long by 0.152 meters wide (34)(35). The resulting long and narrow respirometer covered a benthal area (0.813 m^2) large enough so that small isolated inconsistencies in bottom muds would not cause great variabilities in uptake rates. The long, narrow shape was also required for simulation of actual mixing conditions. In the respirometer designed during this project, velocities typical of a specific test site were generated over bottom muds by recirculating water in the enclosed long respirometer. A flow development section was constructed on the inflow end of the respirometer to distribute the flow evenly over the respirometer cross section. With the volume to area ratio used, reasonable oxygen uptake rates could be measured in four to eight hours. Removable flanges were designed so that the flange portion of the respirometer could be inserted into the bottom deposit some time before the actual respirometer sections were attached. In this way, the bottom deposit was allowed to come to equilibrium before attaching the respirometer sections, pump and sampling hoses. The respirometer sections were made in about 4-1/2 foot lengths and could be installed on the preset flanges at low water. Rubber gasket material sealed all joints between flanges and respirometer sections. Water was recirculated in a 1-1/4 inch PVC pipe using a 1/4 hp submersible impeller-type pump. A 1-1/4 inch brass gate valve regulated pump discharge and therefore the velocity within the respirometer.

The respirometer was attached to the preset sealing flanges at low tide and a typical sampling run was conducted during the time that the area was covered with water within a tidal cycle. Samples, 20 ml in size, were brought to the surface and analyzed in the field for dissolved oxygen using a "Micro-Winkler" modification of the Standard Winkler-Azide method. DO, temperature and salinity were measured both inside and outside of the respirometer. The water removed for the samples was replaced with estuary water through a one-way valve which allowed water to flow only into the respirometer as samples were extracted. The displaced volume for all samples on the longest run was less than 4% of the total respirometer volume. Temperatures were taken in place with thermistors inside and outside the respirometers. Diagrams of the benthal respirometer have been published (34)(35).

To measure the amount of oxygen uptake due to free-floating organisms in the bay-estuary water, planktonic respirometers were developed. Light and dark planktonic respirometers were constructed of three inch diameter plexiglas tubes, six feet in length. A small submersible impeller pump was attached to one end and water was recirculated through the tubular respirometer body at approximately 0.2 feet per second. Exterior hose arrangements used to recirculate the enclosed water were constructed so that the hos could be brought to the water surface for sampling. Methods of dissolved oxygen sampling and analysis were the same as those used for the benthal respirometers.

During the second grant year, a simpler benthal respirometer was also developed and used. This simplified respirometer had attached flanges, was 4 feet long and had a small recirculation pump not capable of producing the higher velocities possible with the large respirometer. Both light and dark respirometers of this type were developed.

Tests indicated that only seven to eight percent of the visible light was obstructed when passing through the 1/8-inch thick plexiglas from which the respirometers were constructed.

MATHEMATICAL MODEL OF BENTHAL RESPIROMETER SYSTEM

To more thoroughly explain and analyze the results of the respirometer study, a mathematical model of the benthal respirometer system was developed. During the early benthal respirometer runs, excessive leakage was evident at site 2. The leakage was found to be principally caused by extensive mud shrimp burrow activity. A mathematical simulation and leakage correction model became a necessity for evaluating leakage as well as helping to determine the importance of different mechanisms or processes of benthal DO uptake. The model was applied to all test runs where salinity data were taken, and corrected DO uptake rates were calculated where leakage existed. Salinity data were used to evaluate leakage rates.

Definition of terms for the following mathematical model are shown in Table 3. The mass balance concept is shown by the following expression.

$$\begin{array}{l} \text{Rate change of sub-} \\ \text{stance mass within the} \\ \text{respirometer volume} \end{array} = \begin{array}{l} \text{Rate of substance} \\ \text{input into the} \\ \text{volume} \end{array} - \begin{array}{l} \text{Rate of sub-} \\ \text{stance output} \\ \text{from the volume} \end{array} \qquad (3)$$

From Table 3 and equation (3), one obtains the following salinity balance:

Salinity Balance:

$$\frac{d(Sr)}{dt} = \frac{(Q)(Sw)}{Vr} - \frac{(Q)(Sr)}{Vr} \qquad (4)$$

It was assumed that the only mechanism of salinity change was by direct leakage into and out of the system and that the volume of the respirometer was constant and completely mixed. Q_1 and Q_2 were assumed to be equal to Q. Some initial changes in salinity might be caused by bottom scour, but such changes that might arise from diffusion of material into or out of the bottom deposit were also considered to be small compared to changes due to leakage; therefore, terms containing Sb do not appear in equation (4).

A similar approach was used to model the changes in oxygen demand (BOD) and dissolved oxygen. The following equations resulted.

Biochemical Oxygen Demand (BOD) Balance:

$$\frac{d(Lr)}{dt} = \frac{(Q)(Lw)}{Vr} - \frac{(Q)(Lr)}{Vr} - (K)(Lr) + \frac{Lbr}{Vr} \qquad (5)$$

TABLE 3. DEFINITION OF TERMS FOR RESPIROMETER MODEL

Term	Units	Description
Q_1	ml/min	Possible leakage into the system.
Q_2	ml/min	Possible leakage out of the system, $Q_1=Q_2$.
Sw	o/oo	Salinity in the overlying water.
DOw	mg/liter	Dissolved oxygen concentration in the overlying water.
Lw	mg/liter	Oxygen demand of the overlying water (BOD).
Sr	o/oo	Salinity in the respirometer.
DOr	mg/liter	Dissolved oxygen concentration in the respirometer.
DOri	mg/liter	Initial dissolved oxygen concentration in the respirometer.
Lr	mg/liter	Oxygen demand of the respirometer water (BOD).
Lri	mg/liter	Initial oxygen demand of the respirometer water.
Vr	liter	Volume of the respirometer.
K	1/min	Decay coefficient of the oxygen demand.
Sb	o/oo	Salinity of the bottom muds and interstitial water.
Lb	mg/liter	Oxygen demand of the interstitial water (BOD).
Lbr	mg/min	Rate of input of oxygen demanding material into the respirometer system from the covered mud area (A).
Ob	mg/min	Rate of oxygen diffusing into the covered bottom mud area (A).
A	m^2	Mud surface area covered by the respirometer.

Dissolved Oxygen Balance:

$$\frac{d(DOr)}{dt} = \frac{(Q)(DOw)}{Vr} - \frac{(Q)(DOr)}{Vr} - (K)(Lr) - \frac{Ob}{Vr} \qquad (6)$$

It was assumed that the rate of input of oxygen demanding material into the respirometer (Lbr) was independent of changes in respirometer BOD (Lr). No measurements were made to determine the interstitial BOD (Lb). Planktonic respirometer studies indicated that Lw was negligible. The diffusion of oxygen into the bottom deposit (Ob) was assumed to be at a constant rate.

CALCULATION OF LEAKAGE

The availability of the benthal respirometer model made possible the calculation of leakage rates for the respirometer system using only salinity data for water in the respirometer and outside of the respirometer. By multiple regression analysis, curves could be fitted to measured salinity data so that the $\frac{d(Sr)}{dt}$, Sw, and Sr could be evaluated at any time. Respirometer volume was a constant value of 60.4 liters. Therefore, all necessary values in the salinity mass balance equation were known, and estimates of leakage rates that occurred could be calculated using equation (4).

DO UPTAKE RATE CALCULATIONS

Equations (4) and (6) were solved using the Runge-Kutta method for finite difference solutions. Fourth order solutions were obtained. Curve fits were used to input required measured quantities such as (DOr), (DOw), (Sr), and (Sw). By solving the salinity equation (4) and the dissolved oxygen equation (6) simultaneously, total oxygen uptake could be calculated by assuming (-K(Lr)-Ob/Vr) to be the unknown rate of benthal oxygen demand exerted within the respirometer. When the build up of BOD within the respirometer and the removal of BOD from the respirometer is small, the total benthal uptake exerted within the respirometer may be divided by the bottom area of the respirometer to obtain the benthal oxygen uptake. Neglect of BOD build up and release will lead to underestimates of the benthal oxygen uptake. Studies indicated, however, that this underestimate was quite small and could be neglected for the reported runs. Corrections could then be made for respirometer leakage. Therefore, even respirometer runs with high leakage rates could be corrected to obtain estimates of the oxygen uptake rates.

During most benthal respirometer runs, slightly more rapid rates of oxygen demand were measured in the first hour of the run than for any succeeding time period. Furthermore, small increases in salinity usually occurred inside the benthal respirometers at start-up. Therefore, during benthal respirometer start-up, water in the respirometer was replaced by disconnecting the return flow pipe at the PVC union and allowing the pump to introduce water into the respirometer. Even then, rapid initial oxygen uptake often occurred. Only DO measurements taken after the initial rapid uptake were utilized in calculating DO uptake rates.

DO UPTAKE RESULTS

Light and dark planktonic respirometers failed to show any measureable oxygen demand or production at either of sites 1,3 and 4. Large mats of phytoplankton often found at site 3 were not included within these runs. Large DO variations, often found in the areas in which these dense growths appeared, indicated that production of dissolved oxygen and respiration by these growths is significant.

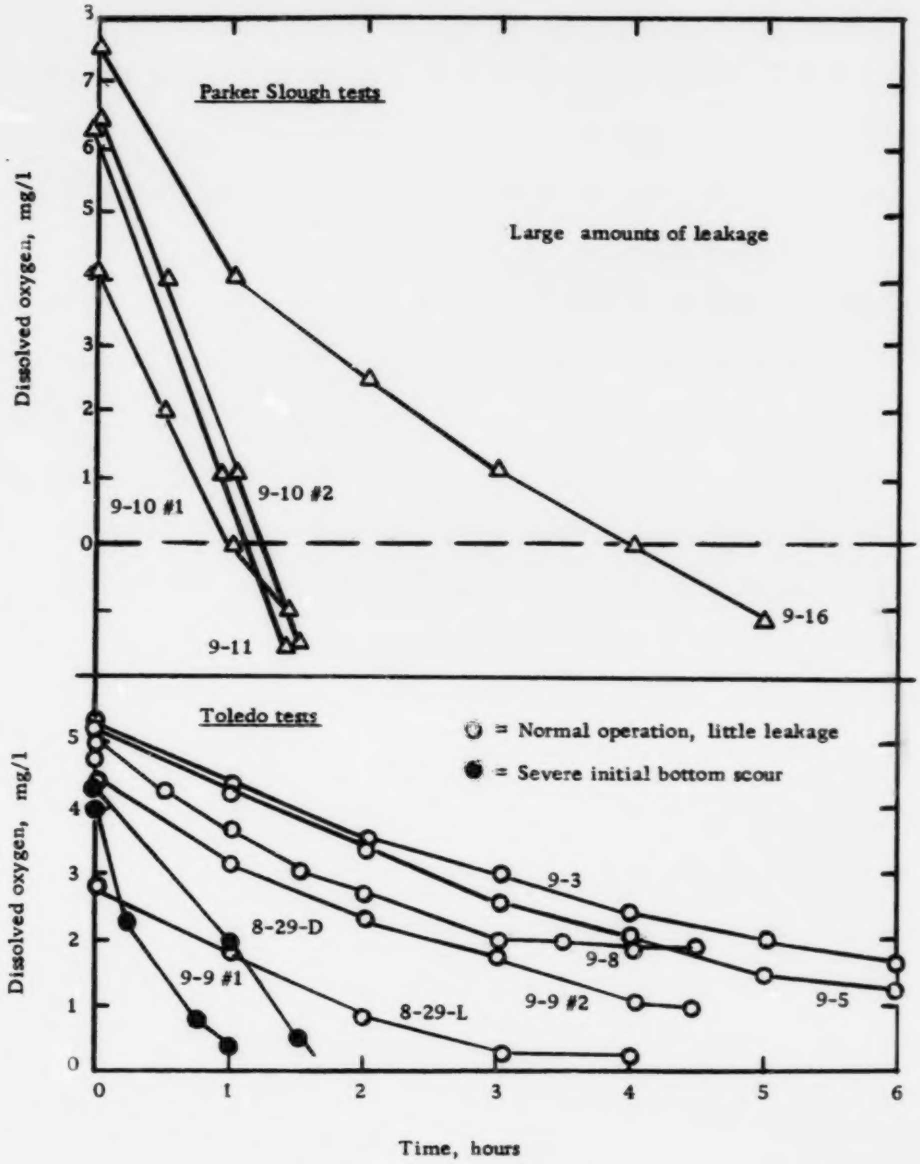


FIG. 6 - SUMMARY OF CORRECTED BENTHAL OXYGEN UPTAKE RATES AT SITES 3 AND 4. (1969)

Using the large dark respirometer, sufficient field data to calculate leakage and uptake rates were collected during four runs at the Parker Slough site and during seven runs at the Toledo test site during the first grant year. The DO changes within the respirometer runs were corrected for leakage as described above (34)(35).

At site 4, benthal uptake rates averaged over each run ranged from 1.4 gm O_2/m^2-day to 2.1 gm O_2m^2-day based on projected surface area. In all runs, the DO uptake rate decreased with time as shown by the decreasing slope of the curves shown in figure 6. Leakage rates and actual DO concentrations within the respirometer also decreased with time. This resulted in apparent relationships between the uptake rate and the DO concentration and water velocity as shown in Fig. 7. Whether these relationships are true or whether they merely reflect the simultaneous occurence of unrelated variations is not apparent at this time.

Table 4 summarizes the average uptake values measured at site 4 for the various mixing velocities used. Table 4 also shows the benthal uptake rates for the same muds measured in the laboratory studies. As can be seen, the in-lab mixed value is slightly higher than the values for benthal oxygen uptake measured during this research. Uncontrolled mixing, sample disturbance, differences in benthal plant respiration or a benthal deposit composition change might all account for these differences in uptake rates.

Excessive benthal respirometer leakage occurred at the site 3 test site as was seen by monitoring the salinity changes in the respirometer water. Leakage rates, calculated by use of the mathematical model, as high as 60 liters per hour were not uncommon. Extreme care during benthal respirometer

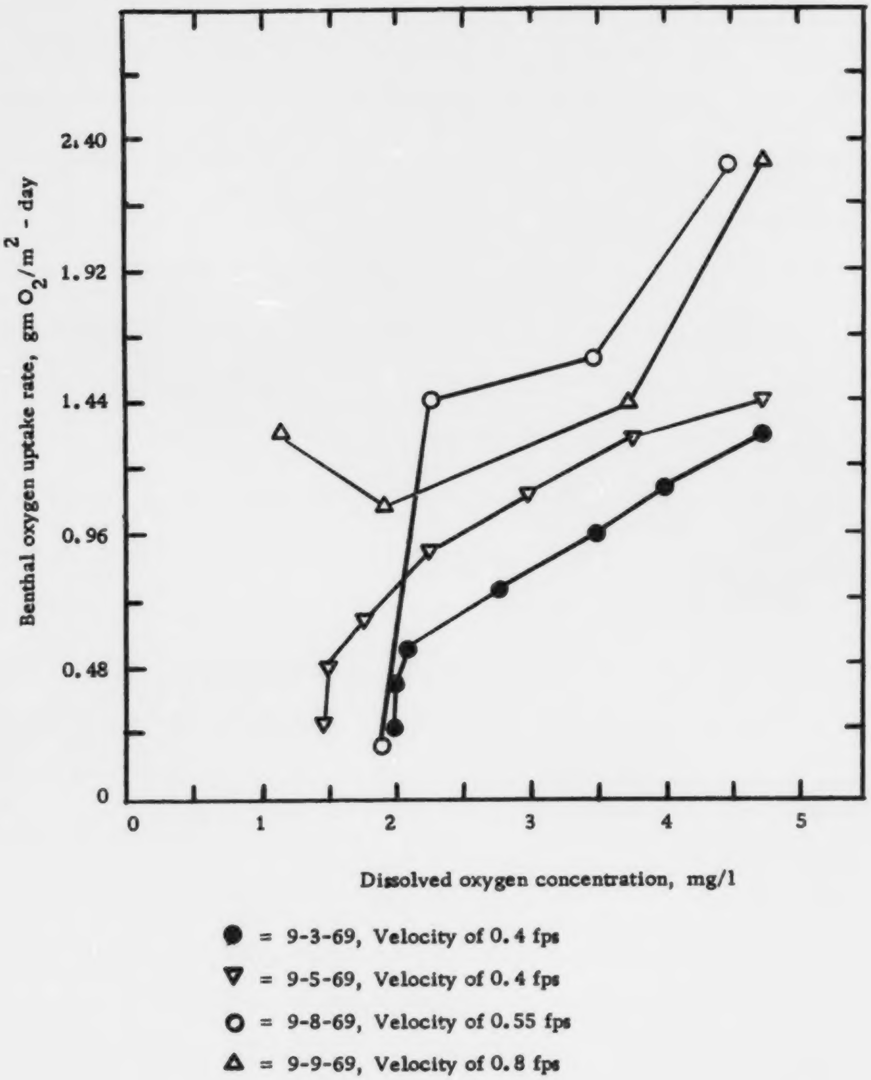


FIG. 7 - VARIATION OF BENTHAL UPTAKE RATES AT SITE 4. (1969)

placement did not result in a significant reduction of the leakage. Dye injections into an operating benthal respirometer at site 3 showed that the respirometer leaks were caused by the numerous mud shrimp burrows that penetrated the area. The mud shrimp burrows apparently formed an interconnecting maze of channels in the tidal flat deposit. On several occasions at low tide, surges of water were observed coming from shrimp holes located upshore from the low tidal water. The observed surges had the same period as small waves breaking against the exposed tidal flat. This further substantiated the inference that the shrimp burrows formed interconnecting networks and could form passages for water circulation.

Computer corrected benthal uptake rates of from 4.8 to 8.5 gm O_2/m^2-day were calculated for site 2. Before correction for leakage rates, comparison of DO changes within the respirometers for the four runs at the Parker Slough site showed little similarity. The rates of DO change were significantly different and increases in the respirometer DO were occasionally measured. After correcting for leakage, the corrected DO changes showed a definite pattern. Three of the runs displayed quite similar uptake rates (see Fig. 6) while the fourth run displayed a lower uptake rate. The leakage rates for this fourth run were quite high and not reliable due to the small measured salinity difference inside and outside of the respirometer. The most reliable results, therefore, indicate that the Parker Slough area displayed an oxygen uptake rate approximately 4 to 6 times greater than that of the Toledo area, or about 8 gm/m^2-day.

Simultaneous measurements using both the dark and light smaller respirometers indicated that the total benthal oxygen uptake depends to a large extent on the respiration of benthal plants. In regions of relatively high benthal photosynthetic oxygenation, as determined by a transparent benthal respirometer, uptake rates of 3 to 6 gms/m^2-day were measured at site 1. At this same site, a lower rate of 1.4 gms/m^2-day was measured in a region of low benthal photosynthesis. These results, in which the smaller respirometers were used are probably not as reliable as results obtained through the use of the larger respirometer.

The larger uptake rates measured at site 3 compared to site 3 (both measured by the large respirometer as previously discussed) appear to be due to the large number of shrimp burrows at site 3 and the larger amount of benthal plant respiration. Though no light respirometer runs were conducted at site 3, the extent of benthal photosynthesis was evident by measured DO concentrations as high as 25mg/l. Also, the bottom at site 3 was observed to be covered with fine bubbles (presumably oxygen) on several occasions. Several respirometer runs had to be rejected because of the release of DO in the form of bubbles within the respirometer. Collection of the gas was attempted with limited success. Therefore, only those respirometer runs in which the DO was sufficiently below saturation to prevent bubble formation were utilized.

A single small dark respirometer run at site 4 measured an uptake rate of approximately 4 gms/m^2-day. A study of DO variation within the overlying water indicated, however, that rates as high as 12 gms/m^2-day might be expected.

Both laboratory and field studies indicated that the DO uptake rate was reduced by 30 to 40 percent when the system was poisoned with mercuric chloride. These experiments, however, were quite limited.

A summary of the principal benthic oxygen uptake rates measured in this study along with examples of rates provided from the literature are summarized in Table 4.

TABLE 4. SUMMARY OF BENTHIC OXYGEN UPTAKE RATE

Reference	DO Uptake Rates gms/m^2 - day	Comments
This study (32) (33)	1.9	Laboratory estuarine sediments, (site 4), low mixing
This study (32) (33)	3.4	Laboratory, estuarine sediments, (site 4), high mixing
This study (34) (35)	1.4	In situ (site 4), estuary, velocity = 0.4 fps
This study (34) (35)	1.7	In situ (site 4), estuary, velocity = 0.55 fps
This study (34) (35)	2.1	In situ (site 4), estuary, velocity = 0.8 fps
This study (34) (35)	4.7-8.5	In situ (site 3) estuary burrow holes present
Mekeown et al (36)	0.8	Laboratory, artificial deposit, no mixing
Mekeown et al (36)	2.7	Laboratory, artificial deposit, mixing
Rolley and Owens (37)	1.2	Laboratory, river muds, frequency distributions provided
Edwards and Rolley (38)	2.8-4.8	Laboratory, river muds, several temperatures, magnetic stirring
Edwards and Rolley (38)	29	Laboratory, river muds, magnetic stirring, bottom scour
Hanes and Irving (39)	3.2	Laboratory, magnetic stirring
Stein and Denison (40)	5-6	Laboratory, Magnetic stirring, some scour
Pamatmat and Banse (41)	0.6-1.2	In situ, Puget Sound, belljar, stirring prop., deep water

TABLE 4. SUMMARY OF BENTHIC OXYGEN UPTAKE RATE (cont.)

Reference	DO Uptake Rates gms/m^2 - day	Comments
Fair et al (42)	1.2-4.6	Laboratory, continuous water flow, artificial deposit, long term
Baity (43)	1.8-5.4	Laboratory, continuous water flow, artificial deposits
Ogurrombi and Dobbins (44)	6-9	Laboratory, artificial deposits, magnetic stirring
O'Connel and Weeks (45)	4.4	Laboratory, artificial deposit, partial scour
O'Connel and Weeks (45)	0.15-8.5	In situ, water current mixed

SENSITIVITY STUDY

To further understand the mechanisms that control benthal oxygen uptake, sensitivity studies were made using the mathematical model previously described. Numerical approximations to the solutions of these equations were obtained by fourth order Runge-Kutta methods. By varying parameters in the dissolved oxygen equation and the BOD equation, curves of oxygen uptake similar to those measured were developed. It was found that, with the equations previously proposed, simulated DO variations corresponded to actual measured DO variations only if a major portion of the oxygen demand was due to one of the following:

A. the transport of oxygen from the water into the deposits,

B. demanding material released from the deposit into the water or

C. combination of A and B from above.

First order decay coefficients, K, needed in assumption B were 10 to 100 times greater than those normally encountered for BOD tests of polluted waters. These results suggest that, under normal water flow conditions, the principal oxygen uptake due to tidal flat deposits occurs in the immediate vicinity of the deposits. Sulfides released from the anaerobic regions could contribute toward such an uptake, though later research indicates that this was doubtful at this location.

It should be recognized, however, that respirometer studies of approximately six hours may be too short to accurately measure the long term release of BOD. High BOD values in tidal flat waters were not found, indicating that such a mechanism was probably not substantial. Accurate measurements of BOD (possibly COD) throughout a respirometer run might lead to better estimates of such release. In general, it was found, however, that the BOD values were too low for sufficient accuracy.

SECTION VII

FREE SULFIDE IN OVERLYING WATER

GENERAL

During the second year of the project, it became apparent that the sulfur cycle was of major importance. From an environmental quality viewpoint, the benthic release of free sulfide was considered to be of major interest for three reasons: (1) Free sulfides exert an oxygen demand, (2) free sulfides are highly toxic to a wide variety of organisms and (3) the release of hydrogen sulfide to the atmosphere could be a major source of atmospheric sulfur.

In order to obtain free sulfides within estuarine benthic deposits it is necessary to have a sufficient production of sulfides, primarily through sulfate reduction, for a long enough duration of time to sufficiently reduce the available iron. Conditions favorable for the presence of benthic free sulfide include high salinity (and thus high SO_4), slight wave and current scour of bottom (to prevent oxidation of ferrous sulfide and "recycling" of iron) and a high organic content within the deposits. Site 5 appeared to best provide all of these conditions; moreover, the bright purple color at portions of the mud surface and under algal mats indicated the presence of photosynthetic purple sulfur bacteria and thus the presence of free sulfides.

Even if free sulfides were present within the deposits, it was questionable at that time if they would be found at levels sufficient for measurement within the overlying water if the dissolved oxygen in this water were not depleted. This question was examined by a number of mathematical models at the same time that analytical methods for measurement of sulfides were examined. The assumptions made to develop these models generally contribute to conservative (low) estimates of free sulfide concentrations in oxygenated waters. The following two sections describe two models used in this portion of the study.

MODEL OF FREE SULFIDE TRANSFER THROUGH AEROBIC ZONE

Consider a vertical column of deposit of cross-sectional area, A. While oxygen demanded substances (free sulfides) diffuse upward, DO diffuses downward from the surface. A second-order reaction between the DO and these substances is assumed. The depth of the deposit, z, is taken as zero at the surface with positive values increasing with depth. The chemical loss rate of DO per unit volume of deposit, G, was taken as

$$G = \mu OCAn\,dz \tag{7}$$

in which

n = the volume of interstitial water within the slice divided by the total volume of the slice,

O = the DO concentration,

μ = the second order reaction coefficient and

C = the concentration of oxygen-demanding material

The diffusive and advective flux, F, of oxygen within the deposit was taken as

$$F = -D_o Am \frac{\partial O}{\partial z} + AqO \tag{8}$$

in which

m = the fraction of the surface area open to diffusion,

q = the water transport rate per unit area, and

D_o = the effective diffusion coefficient for DO.

Performing a mass balance on a segment slice of depth dz and taking A, n, D_o m, and q constant with distance, and A and n constant with time leads to

$$\frac{\partial O}{\partial T} = \frac{D_o m}{n} \frac{\partial^2 O}{\partial z^2} - \frac{q}{n} \frac{\partial O}{\partial z} - \mu OC \qquad (9)$$

As an approximation, both m and n may be taken as equal to the porosity. In the following, advection will be taken as zero. Thus equation (9) reduces to

$$\frac{\partial O}{\partial T} = D_o \frac{\partial^2 O}{\partial z^2} - \mu OC \qquad (10)$$

Similarly, for the oxygen-demanding substances,

$$\frac{\partial C}{\partial T} = D_c \frac{\partial^2 C}{\partial z^2} - \mu OC \qquad (11)$$

is obtained in which D_c is the effective diffusion coefficient for C.

The benthal oxygen uptake, OD', caused by materials included in C, is equal to the sum of the DO flux into the deposit and the flux of C out of the deposit. Thus

$$OD' = \left(D_o m \frac{\partial O}{\partial z}\right)_{z=0} - \left(D_c m \frac{\partial C}{\partial z}\right)_{z=0} \qquad (12)$$

Respiration of benthal algae and oxygen demand of materials not included within C will contribute to the benthal oxygen uptake rate but are not included within OD'.

Approximations to the solutions of Equations 10 to 12 were obtained by explicit finite difference methods. (46) Several runs were also satisfactorily compared with an implicit finite difference scheme.

The relationship between the free sulfide concentration, S, and C will depend on (a) the mass of free sulfides oxidized per mass of DO utilized and (b) the fraction of C caused by free sulfides. As an approximation, S may be taken as 50 to 100 percent of C. Let

$$P_w = \frac{D_c m \left(\frac{\partial C}{\partial z}\right)_{z=0}}{OD'} \tag{13}$$

The model results indicated that P_w ranged from 0.4 to 0.8 with highest values associated with low diffusion coefficients, low oxidation rates (low μ), low dissolved oxygen concentrations in the overlying waters and high benthic oxygen uptake rates. Additional benthic oxygen demand not included in the model would result in a further reduction of DO penetration into the deposit and thus higher values of P_w. Thus, the computed values of P_w may well be underestimates. The results indicate, therefore, that substantially more than half of the upward diffusing free sulfide would be released to the overlying water rather than being oxidized within the deposit.

MODEL OF FREE SULFIDE IN OVERLYING WATER

Consider a vertically mixed column of water of depth H and horizontal area A. A deposit at the bottom of the column has a total oxygen uptake rate given by OD. The upper surface of the water column is exposed to the air, performing a mass balance of sulfides within the column and assuming a steady state leads to

$$S = \frac{Y P_w P_s OD}{HK + K_A f} \tag{14}$$

in which

S = the sulfide concentration,

Y = the mass of S oxidized per mass of DO utilized,

P_s = the fraction of OD resulting from free sulfides formed within the deposit,

K = the first order decay coefficient for free sulfides (equal to $\mu 0$),

K_A = the transfer coefficient of H_2S across the air-water interface and

f = the fraction of the free sulfides present as H_2S.

Because of the simplifying assumptions of equation 14, large differences between computed and observed value, should be expected. Estimates of parameters for equation (14) which might apply to late summer conditions at site 5 are given in Table 5. It is emphasized that these parameters were rough estimates based on a varied and limited amount of information.

The range of free sulfide concentration, S, in the overlying water computed by equation (14) using the parameters shown in Table 5 is enclosed by the solid lines of Figure 8. These results illustrate that significant sulfide concentrations in the overlying water may occur under conditions similar to those found at Site 5.

During the late summer and early fall of 1970, water directly above the sediment of the four sites was monitored during a tidal cycle for dissolved free sulfides and DO. Profiles of DO and free sulfides above the bottom were determined by simultaneously drawing water into six 50-cc plastic syringes attached by small-bore tygon tubing to six 1.5-mm inside diameter stainless

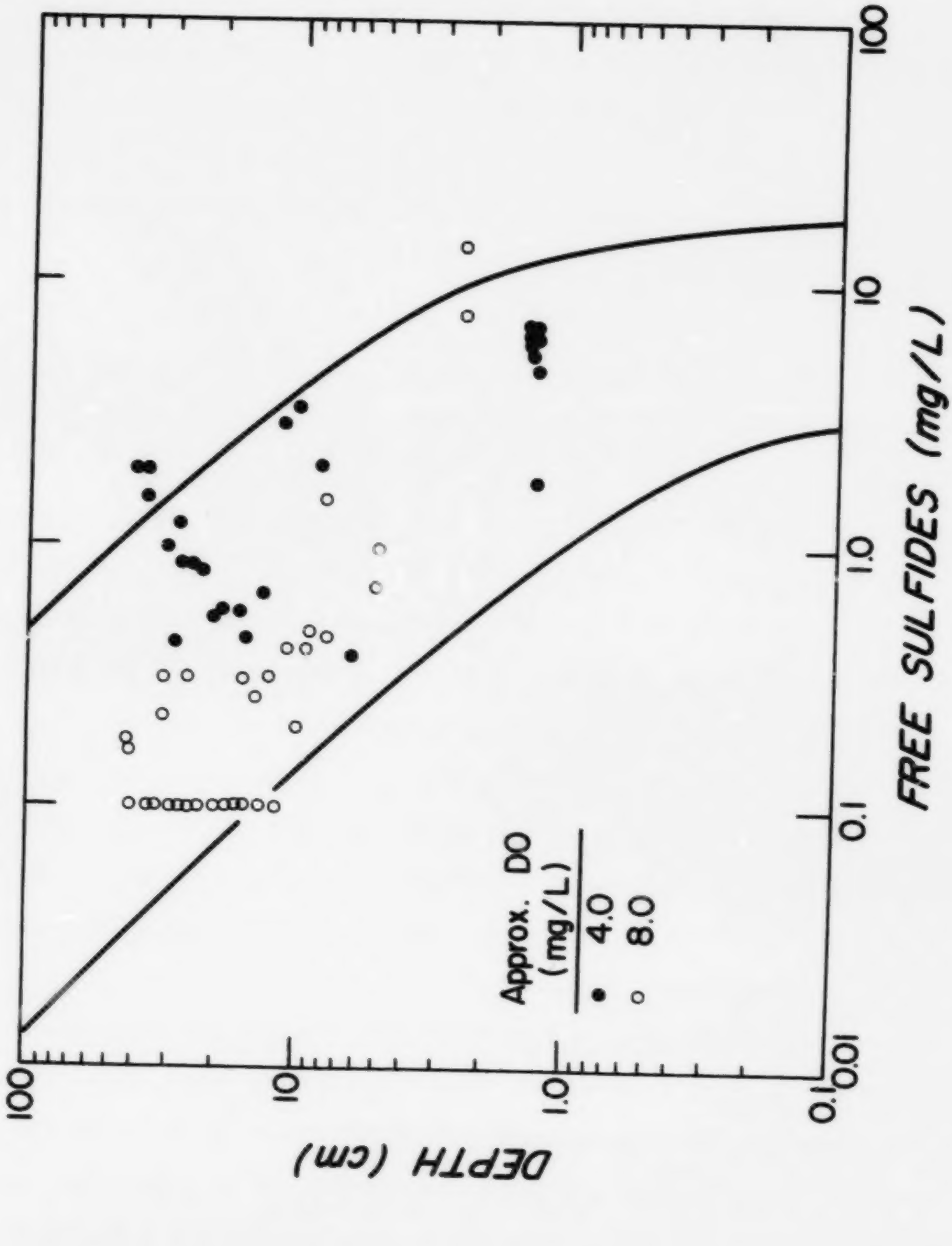


FIG. 8 - RANGE OF FREE SULFIDES IN OVERLYING WATER.

TABLE 5. ESTIMATED PARAMETERS APPLICABLE TO SITE 5 DURING THE LATE SUMMER AND EARLY FALL PERIOD

Parameter	Range	Reference
Y	1.0	(12)
P_w	0.8	This work
P_s	0.3-0.4	(32) (33)
OD	4.0-12.0 (gms/m^2-day)	This work a
K	8.0-70.0 (per day)	(7) (13) (16) b
K_A	0.5 (meters/day)	(58) (59) (46) c
f	0.4-0.5	d

a - estimated from field studies.

b - obtained in sea and brackish water.

c - reference (59) shows similarity between DO and H_2S transfer; reference (58) gives DO transfers for low wind velocities.

d - based on pH of approximately 7 at site 5.

steel tubes set horizontally at varying heights above the deposit. Determination of DO was made on 20-ml water samples collected in 30-cc plastic syringes by a micro-Winkler method (32). Free sulfides were determined by immediately fixing 20 ml of water sample inside the syringe with an equal volume of 50 percent antioxidant buffer solution. The standard solution, which contained 320 g, sodium salicylate, 72 g ascorbic acid, and 80 g sodium hydroxide and made up to 1l in distilled water, prevented further oxidation of sulfide and fixed the free sulfides as essentially all free sulfide ions (6). Sulfide content was then determined by measuring potential on a pH meter equipped with a sulfide membrane electrode and reading the sulfide concentrations from a standard curve developed prior to each run (47). This method was compared with results obtained titrimetrically with iodine (48) and titrimetrically with lead perchlorate using the probe as an end-point indicator (47). Results showed close agreement among all three methods.

The variable ionic strength of estuarine waters was a source of error in the sulfide measurements. Calibration of the probe was done with distilled water with the antioxidant buffer solution and thus reported free sulfide concentrations can be expected to be as much as 20% low. The method of free sulfide determination was later changed to the subtraction method (47) to avoid this problem. Free sulfide and some oxidation products of sulfide can be expected to result in lower measurements of DO. Thus reported DO values may also be underestimated particularly at low DO and high free sulfide values.

Free sulfide and DO profiles measured during daylight conditions at Site 5 are shown in Fig. 9. Because of the benthal photosynthetic oxygenation, DO values were highest near the mud-water interface. Significant free sulfide concentrations were measured despite the relatively high DO values. Higher free

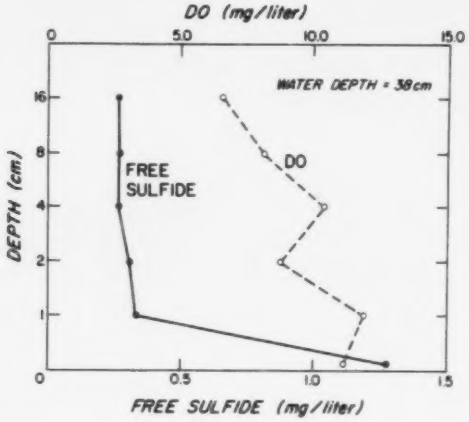


FIG. 9 - DISSOLVED OXYGEN AND FREE SULFIDE PROFILES AT SITE 5

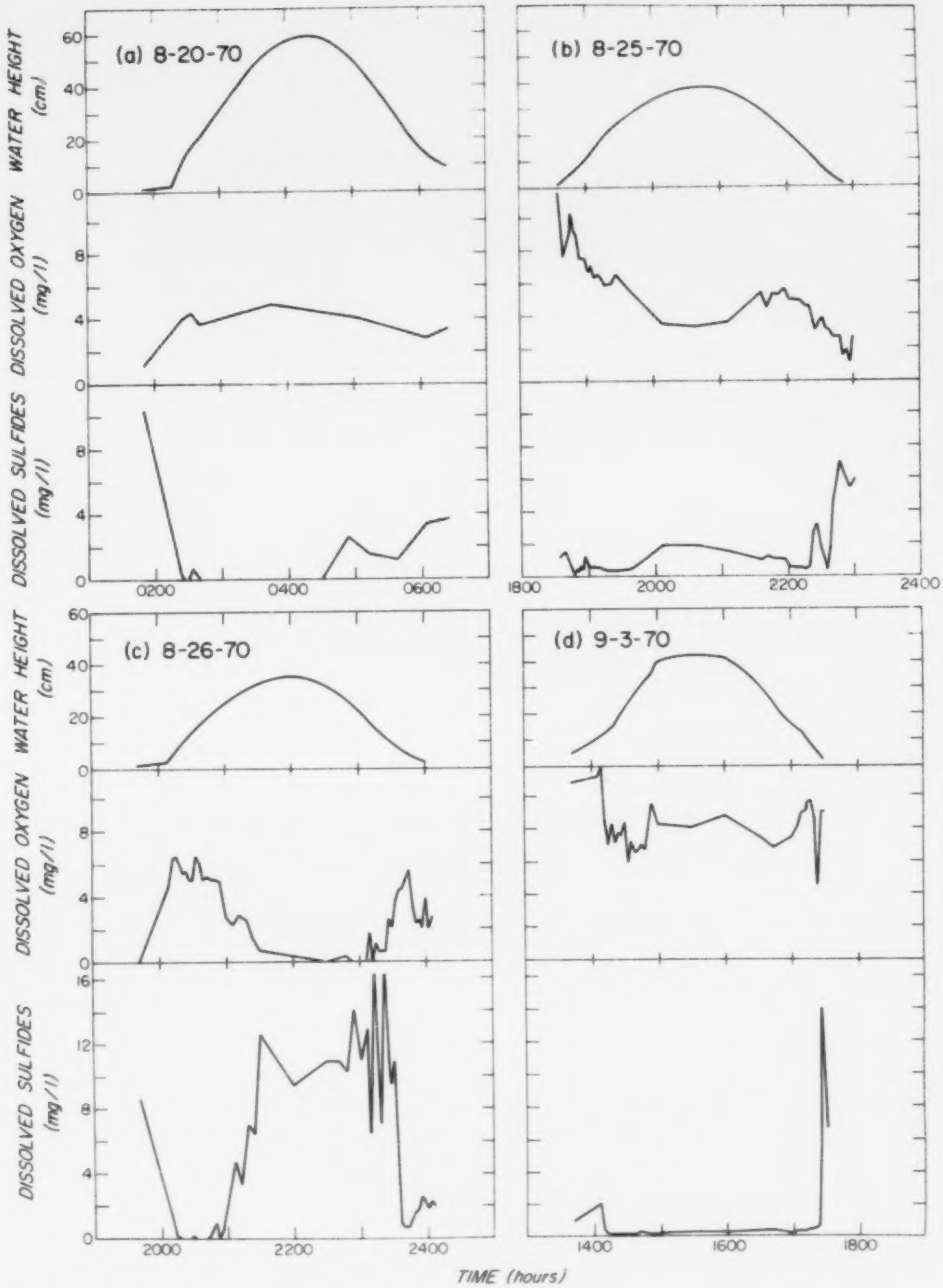


FIG. 10 - DISSOLVED OXYGEN AND FREE SULFIDES AT SITE 5

sulfide concentrations were measured in the low mixed water region immediately adjacent to the mud-water interface.

Results from four sampling periods at site 5 are shown in Fig. 10. Samples for the runs shown in Fig. 10 were collected above the one centimeter distance from the bottom. These results demonstrate the significant free sulfide concentrations can occur in waters at site 5 even in the presence of dissolved oxygen. The relatively stable free sulfide concentrations shown in Fig. 10 are plotted with approximate water depth on Fig. 8. These free sulfide concentrations were within the range roughly estimated by equation 14 and the parameters of Table 5.

Free Sulfide Measurements at Other Sites: Attempts were made to measure free sulfides in the overlying waters of sites 1 and 4. Free sulfides were not detected at site 1. At site 4, free sulfides were detected at low levels (1 mg/1 or less) only for a few samples collected when wave action appeared to disturb the bottoms in the immediate vicinity of the sampling. These occasional measurable levels may have been false readings due to the interference of iron on the sulfide probe. Such measurements at both sites, however, were quite limited and were not sufficient to determine possible seasonal releases of free sulfides.

During the late summer and fall, the *Enteromorpha* and *Zostera* present at site 1 begin to decompose (49). During this same period, redox potentials dropped dramatically in the upper few centimeters of the sediment, microinvertebrates were observed to migrate from the sediments into the overlying algal material, and the smell of hydrogen sulfide was noticeable (49). It is likely that sulfide release may occur at site 1 during this period where benthic algal growth is substantial, however, sampling was not conducted during this period.

SECTION VIII

CONDITIONS WITHIN BENTHIC SYSTEMS

FIELD MEASUREMENTS

While it is true that estuarine benthic systems can strongly influence the overlying air and water quality, they must not be viewed only as a boundary condition of the overlying regions. Benthic systems are of major importance to the total estuarine systems. If they are to be understood, a variety of sediment and water quality measurements must be taken within the benthic systems.

During the final grant year of this project a field investigation of benthic deposits within tidal flat regions was conducted. Sediment cores were collected at sites (usually during low tide) using plexiglas coring tubes. Cores from which interstitial water was obtained were extruded into a plexiglas slicing trough and sliced into desired sections. Sections were immediately placed into field presses so as to prevent chemical oxidation. Interstitial water was extracted in the field within thirty minutes after collection of deposit cores. Four field nylon presses (50) were constructed for this purpose. Pressure not exceeding 150 psi was applied through the use of nitrogen gas. Chemical determinations were either conducted immediately in the field as done with free sulfides or were suitably fixed and determined within several days. Soluble organic carbon (SOC) was measured on a Lira Model 3000 total carbon analyzer. Sulfate was determined by the method of Bertolacini and Barney (51). Free sulfides were determined with a sulfide probe using the subtraction method (47). Chlorides were titrametrically determined (48).

Redox potentials were determined in the field by fixing the cores in a vertical position, placing a reference electrode on the sediment surface and inserting a 1mm platinum wire into the core through small holes drilled at appropriate intervals in the plexiglas core tubes. The reference electrode used was a standard fiber junction reference electrode used in pH, measurements, modified by fastening a fine-frit Gooch crucible about its tip, and filled with saturated potassium chloride solution. Measurements were made following standardization in a solution of known redox potential.

Total sulfides were determined by a modification of the standard titrimetric method (48). Volatile solids were determined by drying and combustion (48). Samples used for total sulfides and volatile solids were kept in the plexiglas cores and cooled or frozen until analysis.

Examples of sediment profiles are shown in Fig. 11. As expected, free sulfides within the interstitial waters were highest at site 5.

A CLASSIFICATION OF ESTUARINE BENTHIC SYSTEMS

Under conditions of relatively constant inorganic and organic inputs, five types of estuarine benthic systems described in Table 6 can develop. These five types are determined by the exogenous hydrogen acceptors available to decompose the deposited organics and the amount of iron (and other metals which form insoluble sulfides) largely from deposited inorganics, available to react with free sulfides. Further subdivision of these five types based, as an example, on the extent of methane fermentation or pyrite formation are possible, but will not be discussed herein.

Fig. 12 qualitatively illustrates the general response of the estuarine benthic systems described above to different continuous inorganic and organic loading rates. The five regions in Fig. 12 correspond to the five types

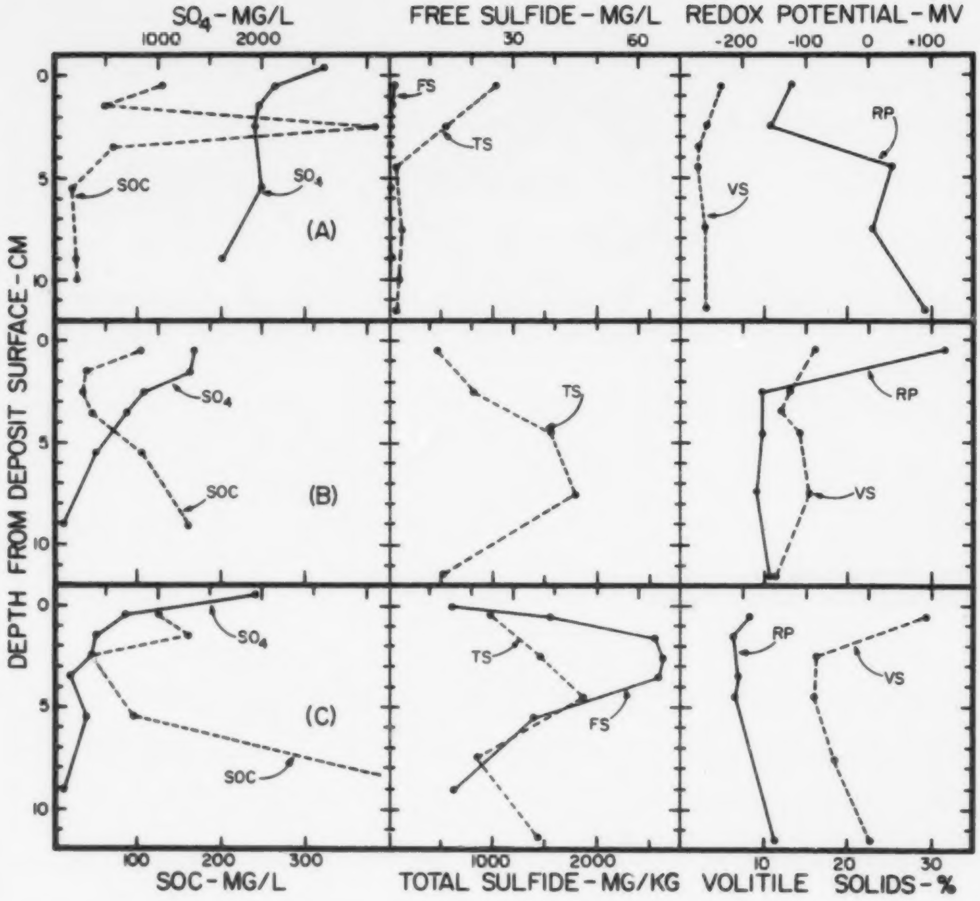


FIG. 11 - EXAMPLES OF ESTUARINE BENTHIC TYPES

TABLE 6. CLASSIFICATION OF ESTUARINE BENTHIC SYSTEMS

Deposit Type	Aerobic Decomposition	Sulfate Reduction	Intersitial Free Sulfide	Methane Fermentation[c]
1	Dominant	Limited (Organic limiting)	Low	Small
2	Significant[a]	Significant (Organic limiting)	Low	Small
3	Significant[a]	Significant (Organic limiting)	Low	Significant
4	Limited to[a,b] Significant	Significant (Organic limiting)	High	Small
5	Limited[a,b]	Significant (Sulfate limiting)	High	Significant[d]

a - Dependent on DO in overlying water.
b - Aerobic zone in deposit limited by free sulfides.
c - Also increased accumulation of organics particularly if conditions are not favorable in Methane Fermentation.
d - Possible inhibition by free sulfides.

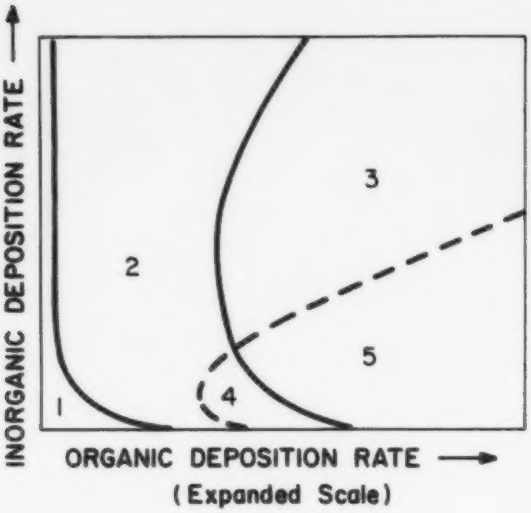

INORGANIC DEPOSITION RATE
ORGANIC DEPOSITION RATE
(Expanded Scale)
1
2
3
4
5

FIG. 12 - QUALITATIVE DESCRIPTION OF ESTUARINE BENTHIC SYSTEM RESPONSE TO CONSTANT DEPOSITION CONDITIONS.

described in Table 6. The solid lines of Fig. 12 are positioned by the availability of hydrogen acceptors while the dashed line is positioned by the availability of iron. The precise quantitative definition of each of these five regions depends upon a wide range of conditions including, but not limited to, the amount of available iron in the inorganics, nature of organics, hydraulic conditions, extent of biological turnover, and concentrations of DO and sulfate within the overlying waters. A quantitative description of each of the regions in Figure 12 is not now possible. Fig. 12, however, does illustrate the general response of the system shown in Fig. 2 to different constant deposition conditions. Qualitative changes in Fig. 12 due to different conditions can be pictured. Larger amounts of available iron within the inorganics, as an example, would lead to clockwise rotation of the dashed line defining regions 4 and 5. Smaller amounts of iron within the inorganics would result in a counter-clockwise rotation of this dashed line. Fig. 11 may not be applicable for very large deposition rates and does not apply well when periodic scour occurs.

Past investigations of marine benthic deposits give some quantitative descriptions of the different regions shown in Fig. 12. Results of the Puget Sound study (52) demonstrated a large decrease of benthic fauna (both in numbers and types) and a strong hydrogen sulfide odor when volatile solids became greater than ten percent of the total solids. This percentage might roughly define, for these locations, the upper bound of region 5 in Fig. 12.

Different benthic estuarine systems will support different sets of plants and animals. The amount of DO available for respiration, the toxic effect of free sulfides, and the amount and suitability of organics for food supply will all serve to determine the nature of resident populations.

Other factors, such as particle size distribution, salinity, and temperature, will also determine the composition of benthic communities.

The regions described in Fig. 12 define the steady state benthic types (shown in Table I) that would be approached if a given set of deposition conditions persisted. The actual types present at a given time are a result of past depositions. Current loading conditions define types which the systems are then approaching. When loading conditions change, systems of one type may shift toward a different type. Seasonal changes of benthic loadings within Oregon estuaries appear to produce seasonal changes of types. Sufficient data, however, are not now available to describe such changes adequately. The data to the date of this report indicate that seasonal scour is an important factor in estuarine benthic systems. The above classification system has the shortcoming that a relatively constant deposition rate is assumed. Where periodic scour occurs, some confusion can result from the use of this classificatio method. A new classification method which accounts for scour is now being developed.

The results presented in Fig. 11 can be used to illustrate three of the five classification systems. Fig. 11A demonstrates an example of a type 2 benthal system (though this system may be approaching type 4). Below the 5 cm depth, organics likely become limited. Free sulfides were detected at low levels (less than 1 mg l^{-1}) only within the top 2 cm of the deposit. Burrows in this region likely contribute toward the transport of oxygenated waters to deeper portions of the deposit. Moreover, water flow through the deposit during low tide likely laterally transported oxygenated water to the deposit. Such transport leads to the oxidation of H_2S and FeS (note positive redox potential of the greater depths). This oxidation can result in the formation of elemental sulfur which may serve as an oxidizing agent leading to the formation of pyrite (53) (note the decrease of total sulfides with depth). The formation of pyrite has not been illustrated in Fig. 1, and the decrease of FeS may have been due to a more complete oxidation.

Fig. 11B presents a type 3 benthal system in which sulfate becomes limiting with depth. The positive redox potential within the first centimeter indicates that aerobic decomposition was likely significant. No detectable free sulfides were measured.

Fig. 11C shows an example of a type 5 benthal system. Sulfate becomes limiting and soluble organic carbon increases at greater depths. Free sulfides within the interstitial waters were measured at levels above 60 mgl^{-1}. The concentration gradient of free sulfides indicates that free sulfides were diffusing upward where oxidation occurred and downward to likely combine with available iron. A negative redox potential was measured throughout the depth. Aerobic decomposition was likely reduced by the upward diffusion of free sulfides.

The highest percent of volatile solids was measured in the type 5 deposit (Fig. 11C) indicating a high organic to inorganic deposition ratio. The lowest such ratio is suggested for the type 2 deposit (Fig. 11A) which had the lowest percentage of volatile solids.

SECTION IX

STUDY OF SULFATE REDUCTION USING EXTRACTS

GENERAL

At approximately the mid-point of this study, it became apparent that the sulfate reduction within estuarine benthic systems was of major interest. Sulfate reduction was examined by three different approaches: (A) Sulfate reduction in organic extracts, (B) Sulfate reduction in mud slurries employing S-35 tracer and (C) incubation and measurement of entire benthic cores. Due to time constraints, the major investigative effort was given to method A.

As previously discussed, the major producers of free sulfides in marine and brackish water appear to be sulfate reducing bacteria. Those organisms, belonging chiefly to the genus Desulfovibrio, are ecologically quite versatile, and are ubiquitously distributed in nature (54). They occupy habitats embracing a wide range of pH, salinity, Eh, temperature, and osmotic and hydrostatic pressure.

Most cultures, however, appear to grow best between a pH of 6.2 and 7.9 and an Eh of -50 to -150 mv (54). Sulfate reduction itself tends to lower Eh and raise pH of environments in which it occurs, the magnitude of such effects depending upon the buffering capacity of the medium, and the end-produc of the oxidation-reduction process (54).

Based upon salinity tolerance, there appear to be two general, although somewhat indistinct, physiological types. Those found within soil, sewage, and fresh water are most active in solutions of less than one percent sodium chloride, and become inhibited at 1.5 - 3.0 percent concentrations. The other group, occurring in marine and brackish waters, appears to require sodium chloride solutions isotonic to sea water or sea water itself (54).

The trace mineral requirements of these organisms are but imperfectly known and probably quite variable. Ferrous iron is essential, due to the presence of a cytochrome system in species of Desulfovibrio (55).

Growth of sulfate reducers has been observed at temperatures ranging from -11° to 104°C, but the majority occur in the ocean floor sediments at temperatures below 5°C. They appear to grow best at 15 - 40°C(81).

The organic acids as a group (lactate, pyruvate, maleate, citrate, propionate) appear to be the most readily available and preferred energy source for sulfate reducers (54). In addition, fatty acids, simple alcohols, and some mono and disaccahrides are suspect. Complex carbohydrates do not appear to be directly utilizable, but the importance of other microorganisms in the breakdown of these to utilizable forms has been noted (56).

Sulfate ions appear to be by far the most common hydrogen acceptor (55). They are usually in abundant supply in sea water, and there is good evidence that the process of sulfate reduction may have been dominant and had global implications during past eras (57). There is some evidence suggesting that sulfate reduction is not limited until the sulfate concentration drops below 10 mg/l, but it is probable that halophilic strains become limited at higher concentrations. In estuaries, sulfate reduction in bottom deposits is dependent on both a supply of sulfate and organic material within the interstitial and overlying waters, and sulfate may become limiting at the head, and organic material limiting at the mouth of estuaries (31).

In addition to sulfates, the use of sulfite, thiosulfate, hydrosulfide and several other sulfur oxides, as hydrogen acceptors, has been demonstrated (54). These compounds, however, are not generally widely available in nature, and are considered to be of considerably less significance. Since more energy is derived from the more oxidized form, it is probable that it would be preferentially utilized when available. The ability of sulfate reducers to utilize elemental sulfur is questionable (55,54). Some autotrophic strains are apparently able to utilize carbon dioxide and the bicarbonate ion as a hydrogen acceptor (54).

The question of whether the activity of sulfate reducing bacteria in nature and in synthetic media is affected by the hydrogen sulfide (or other free sulfide) produced has been examined by several investigators (54,55,60). It appears that the levels of free sulfide which may be tolerated are critically dependent upon pH, available sulfate, the nature of the energy source, and the presence of cations which may form insoluble sulfides (54).

MEDIA PREPARATION

Sediment extract media were prepared as follows from sediment collected from the upper five centimeters of deposits.

A. One liter of distilled water was added to one liter of sediment in a large erlenmeyer flask, thoroughly mixed, and the resulting slurry autoclaved for 45 minutes at 121°C. After removal from the autoclave, the slurry was allowed to cool and the sediment removed by centrifugation. The resulting clear extract was either utilized directly as growth media, or lyophilized to produce a powder. In some cases this powder was added to liquid medium to yield one of higher organic concentration. Sulfate concentration were increased by addition of sodium sulfate, or decreased by adding barium chloride. The pH was adjusted to near neutral by addition of sodium hydroxide.

B. One liter of sea water was added to one liter of sediment and treated as with the addition of distilled water as described in method A.

C. One liter of either three or ten percent hydrochloric acid was added to one liter of sediment and treated as with the addition of distilled water as described in method A.

Algal Extract Media were prepared from the algal mat collected at site 5 by the following methods:

D. Two liters of algae and its associated water were placed into a three liter erlenmeyer flask and autoclaved as with sediment media. Following cooling, the algal material was squeezed using a wooden fruit press, and the liquid collected and centrifuged. Sulfate concentrations and pH of the media were adjusted as previously described.

E. Approximately 250 ml of 10 percent hydrochloric acid was added to 500 ml of algae and treated similar to that in method D.

F. Small amounts of liquid were extracted from both sediment (collected from the upper five centimeters at the sites) and algae (site 5) by using a hydraulic press and specially designed squeezing cylinder. In addition, approximately one liter of extract was prepared by squeezing by hand algae which had been freshly collected from site 5.

The results of preparing media by the various methods of organic extraction are summarized in Table 7. Early attempts at preparing media

TABLE 7. SUMMARY OF SOLUBLE ORGANIC EXTRACT PROCEDURES

Sample Material	Extraction procedure	Soluble organic(a) carbon (mg/l)	Sulfate(a) (mg/l)
Site 1 - sediment	A(b)	150 - 250	nm.(c)
	C(b)	150 - 300	nm.
	F (b)	50	3200
Site 2 - sediment	B	100 - 150	nm.
	A	100 - 800	10 - 300
	C(b)	3200	nm.
	F(b)	60 - 110	100
Site 3 - sediment	A(b)	200 - 300	200
	C(b)	1600 - 3400	1400
	F(b)	140 - 310	1000 - 1500
Site 3 algal mat	D	1500 - 3000	3400 - 4000
	E(b)	5400	nm.
	F(b)	2010	4800
	F(hand squeezed)	1125	2150

(a) Approximate.

(b) These extracts not used for media.

(c) Not measured.

from sediment (methods A and B) inevitably resulted in media having fairly low organic carbon concentrations (100-800 mg/l). Extraction methods with acid resulted in higher concentrations of organic carbon, but a large percentage of this organic carbon precipitated out upon adjustment of the pH with sodium hydroxide to neutral. Hence little was gained in the final media by using acid extraction.

An analysis of sugars and organic acids was performed on a number of extracts. The general results indicated that the pentoses present at site 4 likely reflected the input of wood products to this area. Sediment extracts from site 1 showed small amounts of both pentoses and hexoses suggesting that the organic material there may come from more diverse sources. The relatively lower levels at site 1 reflect the lower organic concentrations measured here. At site 5 high concentrations of mannose and glucose, both hexoses, as well as high levels of propionate, butyrate, and acetate were present.

METHODS

A number of experimental approaches were attempted in this study. Only the last approach, which took advantage of previous experience, is reported.

Approximately 600 ml of algal extract medium (prepared according to method D) were placed into each of twelve 500 ml erlenmeyer flasks, organic concentrations adjusted by dilution, and desired sulfate levels achieved as previously described. Sodium chloride was added where necessary to adjust the chlorinity of each culture to approximately 20 ppt. Two additional cultures were similarly prepared using media prepared by hand squeezing algae from site three. Oxygen was initially removed by sparging for 15 minutes with carbon dioxide-free nitrogen. The pH was then adjusted to 7.5 - 8.0 by addition of 3.0 N sodium hydroxide, and Eh lowered to approximately -1[illegible] mv by addition of a small quantity of sodium sulfide. Each flask was inoculated with two ml of mixed culture and immediately capped by a rubber stopper fitted with a glass tube and serum cap. To prevent leakage, modeling clay was liberally applied around the edges, and the stopper further fastened down by masking tape. Each flask was shaken to disperse the inoculum, and initial samples were taken for analysis. The flasks were then incubated in the dark at 20°C. A control was set up by filling several tubes with sterile extract, and capping tightly. No significant changes were measured in the control series.

Samples were withdrawn from the flasks at appropriate intervals with a syringe which had been flushed and prefilled with nitrogen. By exchanging the gas for the sample, the flask was maintained anaerobic and development of a negative pressure due to extraction of the samples was avoided. Flasks were shaken thoroughly prior to sampling in order to produce a fairly homogeneous medium, giving a more representative sample. Total sulfide was measured by adding 10 ml of sample to a known volume of acidified 0.025 N iodine solution and back-titrating with 0.025 sodium thiosulfate.

Sulfate was determined by a colorimetric procedure using barium chloranilate (51). Samples were passed through a Dowex 50w-x8 20-50 mesh H^+ cation exchange column to remove interferring ions, diluted to 40 ml if necessary, and added to 50 ml of 95 percent ethanol and 10 ml potassium phthalate buffer. Approximately three grams of barium chloranilate were added to precipitate the sulfate. After shaking for ten minutes, the solution was filtered, and the optical density determined on the filtrate with a spectrophotometer. Sulfate concentrations were read from a standard curve.

Soluble organic carbon was used as a measure of the soluble organic material present. Five ml of centrifuged sample were placed into 20 ml screw cap test tubes in an ice bath, and carbonate carbon removed by acidifying to pH 2.0 - 3.0 with three percent phosphoric acid and sparging with carbon dioxide-free nitrogen for 10 minutes. Determination of the remaining soluble organic material was made using a Lira Infrared Analyzer Model 3000. Eh was measured with a platinum wire electrode, and pH with indicator paper. Fourteen cultures were run.

Cultures 1 through 12 contained media prepared from autoclaved algae (method E), whereas cultures 13 and 14 contained media prepared from squeezed unautoclaved algae (method F). During the initial portions of each run, sodium hydroxide was added to maintain a satisfactory pH. After several days, stable conditions of pH and Eh were achieved, further addition of base became unnecessary, and active sulfate reduction began to occur. Day 0 (zero) of the experiment was set when the pH and Eh became stabilized. This occurred three to five days following inoculation.

RELATIONSHIP BETWEEN SULFIDE, SULFATE, AND ORGANIC CARBON

Dissimilatory sulfate reduction requires an organic source for energy, and sulfate as a hydrogen acceptor (20,55). The stoichiometric relationship for sulfate reduction is given as (20)

$$\underset{-(12)}{SO_4^{=}} + \underset{-(3)}{2C_{organic}} \rightarrow \underset{+(4)}{S^{=}} + 2CO_2 \qquad (15)$$

where the numbers below the chemical formulas indicate the reaction on a weight basis. Thus during sulfate reduction, a production of 1.0 mg of sulfide will theoretically require 3.0 mg of sulfate and 0.75 mg of organic carbon. These 'yield ratios' have been calculated for the mixed cultures

TABLE 8. EXPERIMENTAL YIELD RATIOS AND MAXIMUM RATES OF SULFIDE PRODUCTION FOR EACH CULTURE[a]

Culture No.	Y_{sul}[b]	Y_{soc}[c]	V_{max}[d]	Sulfate Limitation
1	3.2	0.82	54	No
2	3.0	0.89	60	Slight
3	3.0	1.60	54	Slight
4	3.2	2.00	48	Large
5	3.0	2.30	35	Large
6	3.4	6.05	10	Large
7	3.1	0.86	70	No
8	3.2	0.86	62	No
9	3.0	0.91	51	No
10	3.2	0.80	30	No
11	3.0	0.88	20	No
12	3.1	1.10	10	No
13	3.1	0.94	54	No
14	2.9	0.84	34	No
Theoretical	3.0	0.75	--	

(a) Yield ratios (Y_{sul} and Y_{soc}) calculated over the 14 days of the experiment.

(b) (mg/l of sulfate utilized) / (mg/l of sulfide produced).

(c) (mg/l of soluble organic carbon utilized) /(mg/l of sulfide produced)

(d) The maximum rate of sulfide production (mg/l-day) as measured over three day intervals, during the 14 days of the experiment.

over the 14 days of experiments, and are presented in Tables 8 and 9 where

$$Y_L = \frac{\text{mg/l of sulfate consumed}}{\text{mg/l of sulfide produced}} \tag{16}$$

and

$$Y_C = \frac{\text{mg/l of soluble organic carbon consumed}}{\text{mg/l of sulfide produced}} \tag{17}$$

It is important to recognize that these yield ratios reflect the activity of all the bacteria within the mixed cultures of the experiment and not just the sulfate reducers.

TABLE 9. SUMMARY OF YIELD RATIOS

	Sulfate/sulfide Y_L	Carbon/sulfide Y_C
Theoretical	3.0	0.75
Average overall runs	3.1	1.49
Average overall runs with no sulfate limitation	3.09	0.89

Agreement between the theoretical value of Y_L for sulfate reduction and the values of Y_L determined from the experiment was good. The slightly higher experimental values may be due in part to assimilatory reduction of sulfate during initial growth of all of the bacteria present in the cultures.

Y_C was more variable than Y_L and exceeded the theoretical value of 0.75 in every culture. Since these mixed cultures contain bacteria other than sulfate reducers, which are capable of utilizing the organic carbon, this result is not surprising. That these other bacteria are capable of such utilization was apparent from the drop in soluble organic carbon in the absence of measurable sulfate reduction prior to day 0. In general, where sulfide production became curtailed by deficiency of sulfate, the value of Y_C increased well above the theoretical, as would be expected.

RATES OF SULFATE REDUCTION

The agreement between the theoretical and experimental yield ratios shown in Tables 8 and 9 indicate that sulfate reduction was responsible for the sulfide production measured. The maximum rate at which this sulfate reduction occurred (expressed as mg. of sulfide/1-day) in the extract experiments is shown (V_{max}) in Table 8. Rates have been estimated over a three day interval in each culture in which the maximum rate appeared to be occurring.

Results obtained in cultures 9 and 10 correspond closely to those of culture 13 and 14 respectively. (see Figs. 21, 22, 25, 26, and Table 8). This close agreement indicates that the effect upon sulfide production of autoclaving the algae used in the preparation of cultures 1 through 12 was not significant. The media for cultures 13 and 14 were obtained by hand squeezing the algal mat found at site 5.

To further explain the results of the extract experiments a mathematical model was used which relates the production of sulfide to the utilization of sulfate and soluble organic carbon. Results indicated that the sulfide production rate increased as the concentration of sulfate and/or organic carbon increased. This effect, however, was most pronounced at lower levels of sulfate and carbon, and became relatively small at higher concentrations. An equation which has been used to describe such a saturation effect at high substrate concentrations is the common Michaelis-Menton equation shown below:

$$\frac{dP}{dT} = R_{max} \left(\frac{N}{K_s + N}\right) \qquad (13)$$

in which P is the concentration of the product, R_{max} the maximum rate of product formation, N the substrate concentration, and K_s the substrate concentration at which $dP/dT = 1/2\ R_{max}$.

With sulfate and soluble organic carbon serving as substrates, the rate of sulfide production may be expressed as

$$\frac{dS}{dt} = R_{max} \left(\frac{L}{K_L + L}\right) \left(\frac{C}{K_C + C}\right) \qquad (19)$$

where L is the sulfate concentration, C the soluble organic carbon concentration, and K_L and K_C the Michaelis coefficients for L and C respectively. Bacterial populations are assumed to be relatively high and stable.

Since sulfate and soluble organic carbon are being consumed in the production of sulfide, their rate of utilization may be expressed as

$$\frac{dL}{dt} = -Y_L \left(\frac{dS}{dT}\right) \qquad (20)$$

and

$$\frac{dC}{dt} = -Y_C \left(\frac{dS}{dt}\right) \qquad (21)$$

The value for Y_L for use in the model was obtained by averaging the measurements of this yield coefficient for cultures 1 through 12 (Table 8). Y_C was similarly obtained, but by weighting most heavily those values of Y_C from cultures which were not markedly sulfate limited during the experiment. Measurements from cultures 13 and 14 were not included in the average since these cultures were prepared with unautoclaved media.

Initial comparison of experimental results with calculated results of equations 19, 20 and 21 demonstrated that production of sulfides responded more sharply to changes in sulfate concentrations at low sulfate concentrations than is described by the traditional Michaelis-Menton equation. This sharper response could be expressed within the model by raising the sulfate concentration in equation 8 to higher powers. Based on simulation of cultures 3 through 6, it was decided to raise the sulfate concentration to the 1.3 power, thus replacing equation 19 by

$$\frac{dS}{dt} = R_{max} \left(\frac{L^{1.3}}{K_L' + L^{1.3}}\right)\left(\frac{C}{K_C + C}\right) \qquad (22)$$

Estimates of R_{max}, K_L' and K_C were obtained using multiple nonlinear regression analysis to fit the combined data of cultures 1 through 12 to equation 22. Since the model assumed no lag in sulfide production, data for the first one to two days of those cultures in which an obvious lag occurred was not included in the analysis.

The result of the regression indicated a maximum rate of sulfide production (R_{max}) of 77 mg/l day. The values of K_L' and K_C were 320 mg/l and 650 mg/l respectively. A value of 3.1 was used for Y_L and 1.0 for Y_C. The resulting equations with the fitted parameter estimates are shown below:

$$\frac{dS}{dt} = 77 \left(\frac{L^{1.3}}{320 + L^{1.3}}\right)\left(\frac{C}{650 + C}\right) \qquad (23)$$

$$\frac{dL}{dt} = -3.1\ (\frac{dS}{dt}) \qquad (24)$$

$$\frac{dC}{dt} = -1.0\ (\frac{dS}{dt}) \qquad (25)$$

Approximations to the simultaneous solutions of equation 23, 24 and 25 were obtained by digital computer using a fourth order Runge-Kutte finite difference method. The simulations of cultures 1 through 12 are shown in Figs. 13 through 24. Solid lines represent the values of sulfide, sulfate, and soluble organic carbon calculated by the mathematical model. Circles are the data taken from the respective cultures of the experiment. The values of pH and Eh indicated are from the experiment.

Agreement between simulated and measured results are especially good for those cultures in which the rates of sulfide production were highest. Agreement was in general best for sulfide and sulfate, while the calculated concentrations of soluble organic carbon deviated more from the experimental measurements. The selection of a Y_C of 1.0 for the simulation model is reflected in these results. The average value obtained for those experiments in which sulfate was not limiting, 0.89, would have resulted in closer agreement except where sulfate became limiting. Part of the difference between the simulation and experimental results can be attributed to the lag period which occurred in many of the cultures from day zero to one. It will be recalled that the model assumes no such lag, and that data for this lag was not included in the regression analysis. Excluding the lag period from Figs. 13 through 26 by considering day one the beginning of the experiment, would result in a much closer agreement of simulated with measured results in most cultures.

Equations 23, 24, and 25 were used to simulate production of sulfide and consumption of sulfate and soluble organic carbon in cultures 13 and 14 (see Figs. 25 and 26. Simulated sulfide production was within 10 percent of the actual production. Soluble organic carbon consumption was under-estimated as with simulations of all cultures having a Y_C less than 1.0. A value of 0.89 would have provided closer agreement.

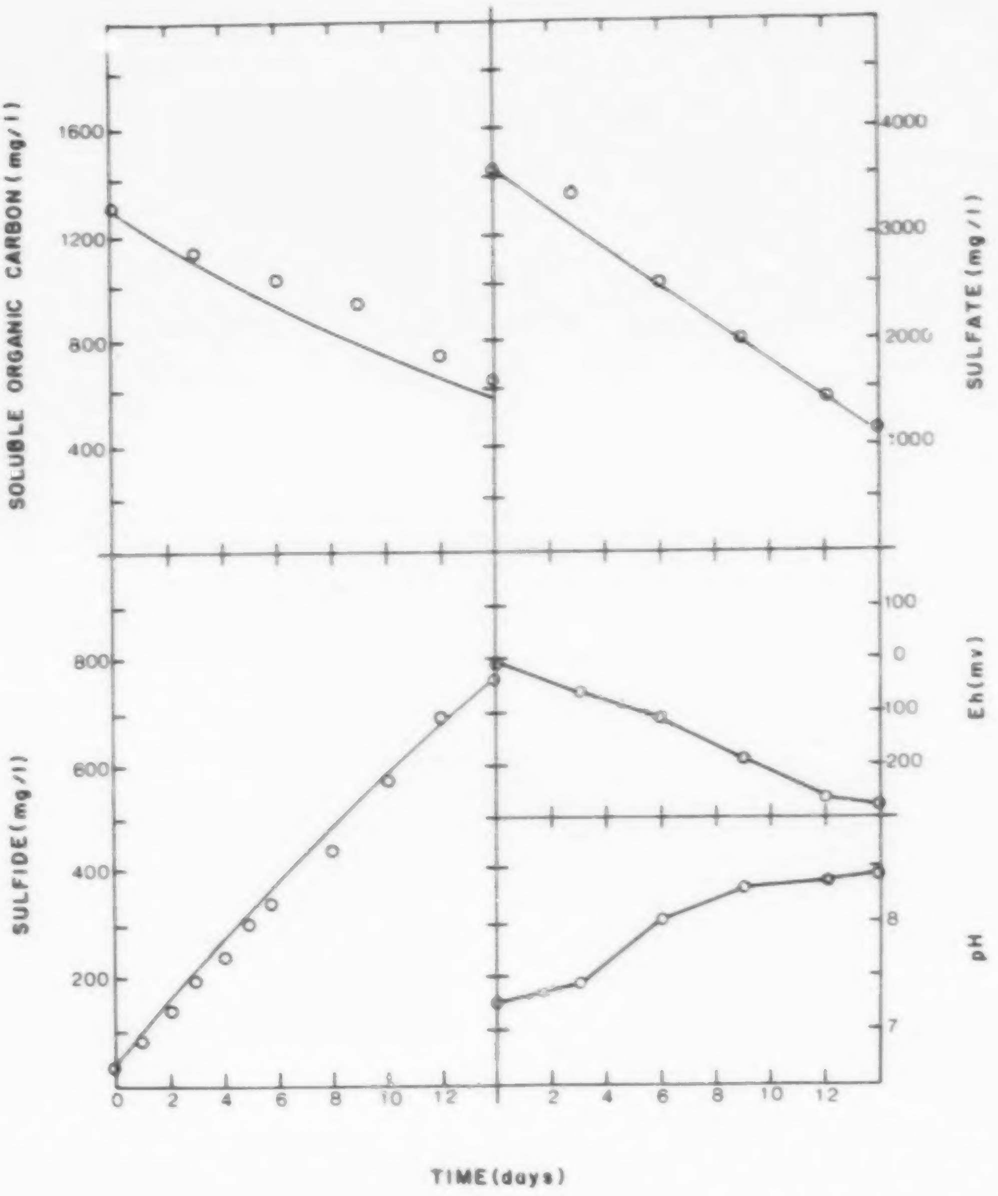


FIG. 13 - EXPERIMENTAL RESULTS OF CULTURE 1 COMPARED WITH EQUATIONS 23, 24, and 25.

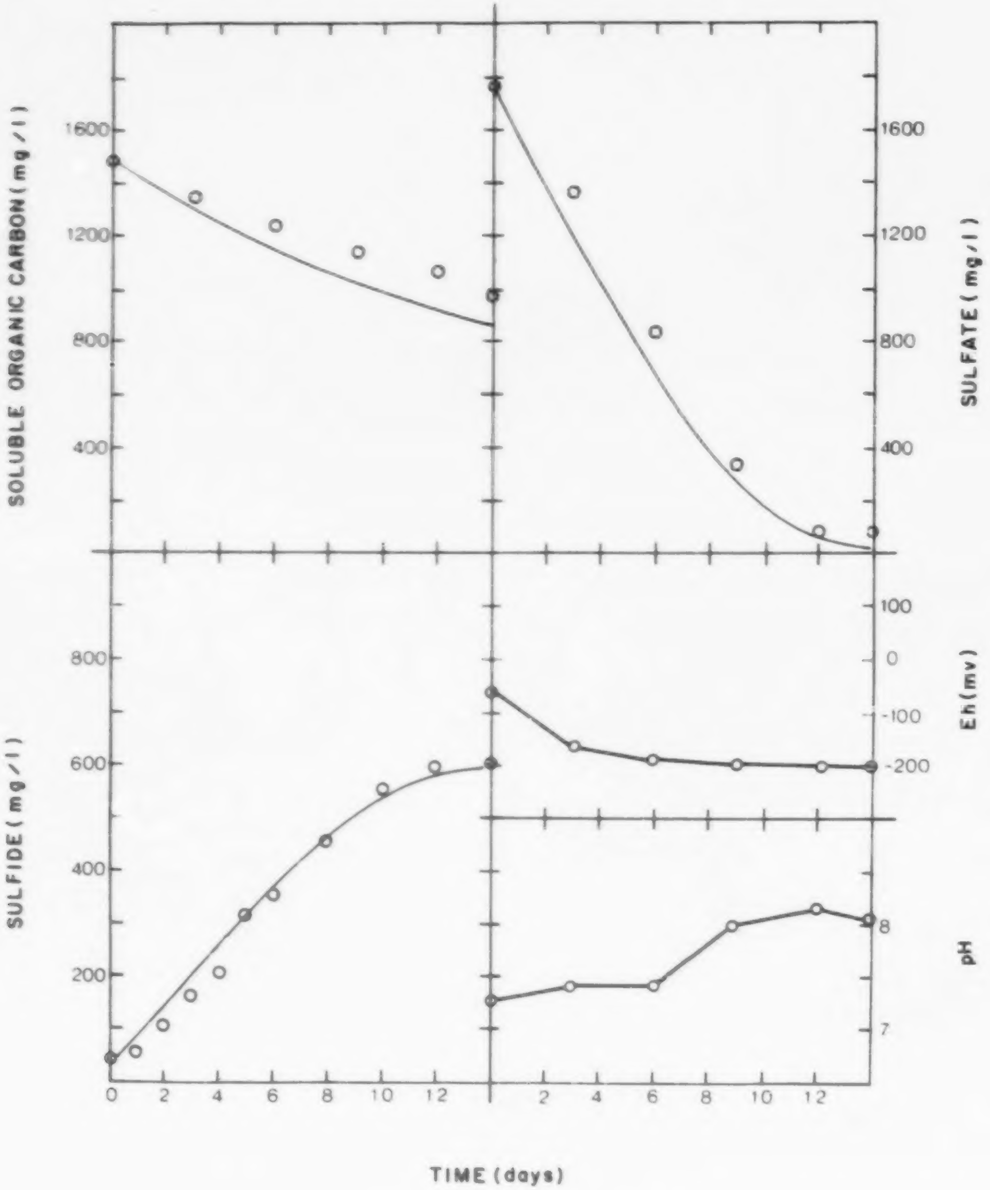


FIG. 14 - EXPERIMENTAL RESULTS OF CULTURE 2 COMPARED WITH EQUATIONS 23, 24, and 25.

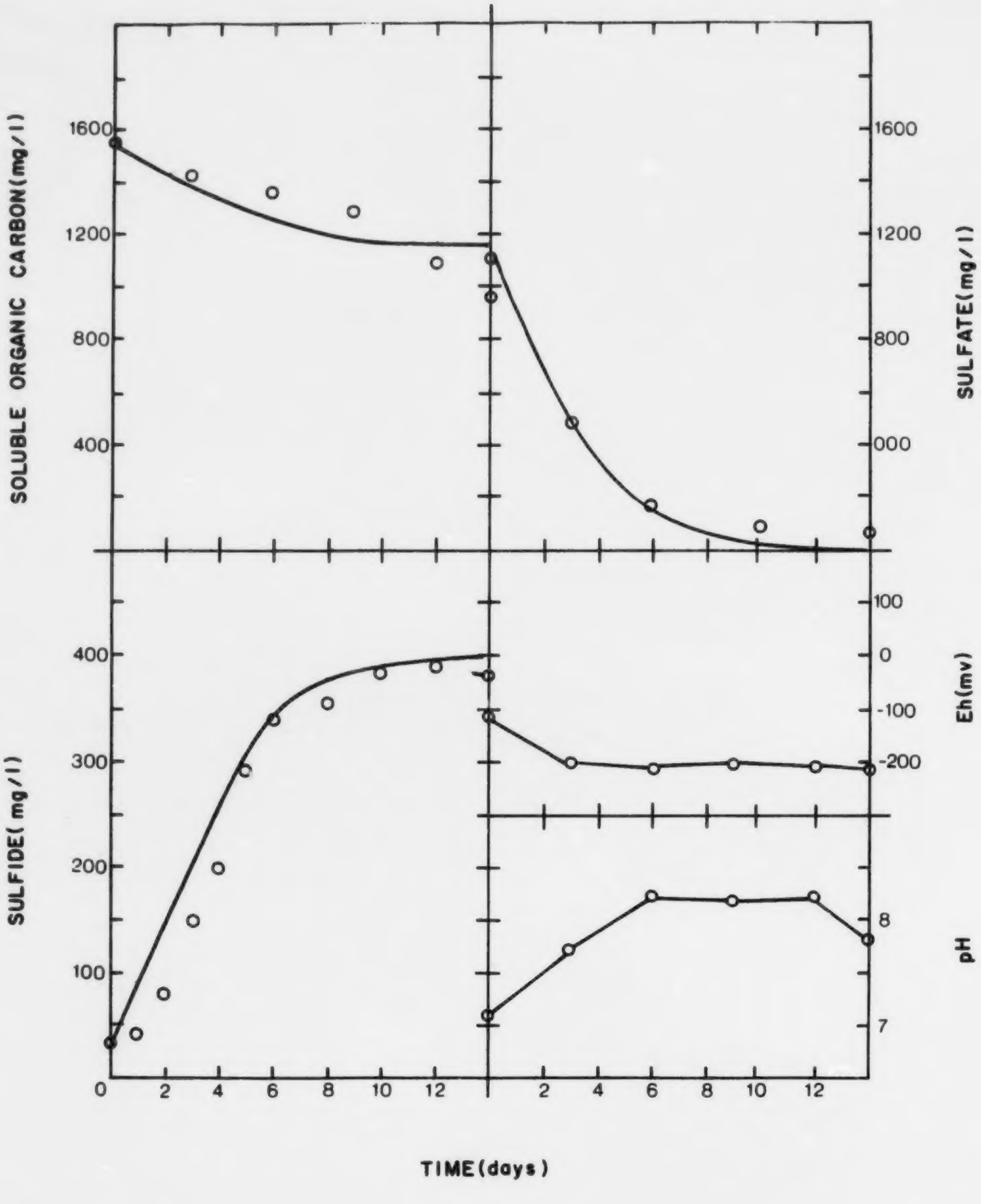


FIG. 15 - EXPERIMENTAL RESULTS OF CULTURE 3 COMPARED WITH EQUATIONS 23, 24, and 25.

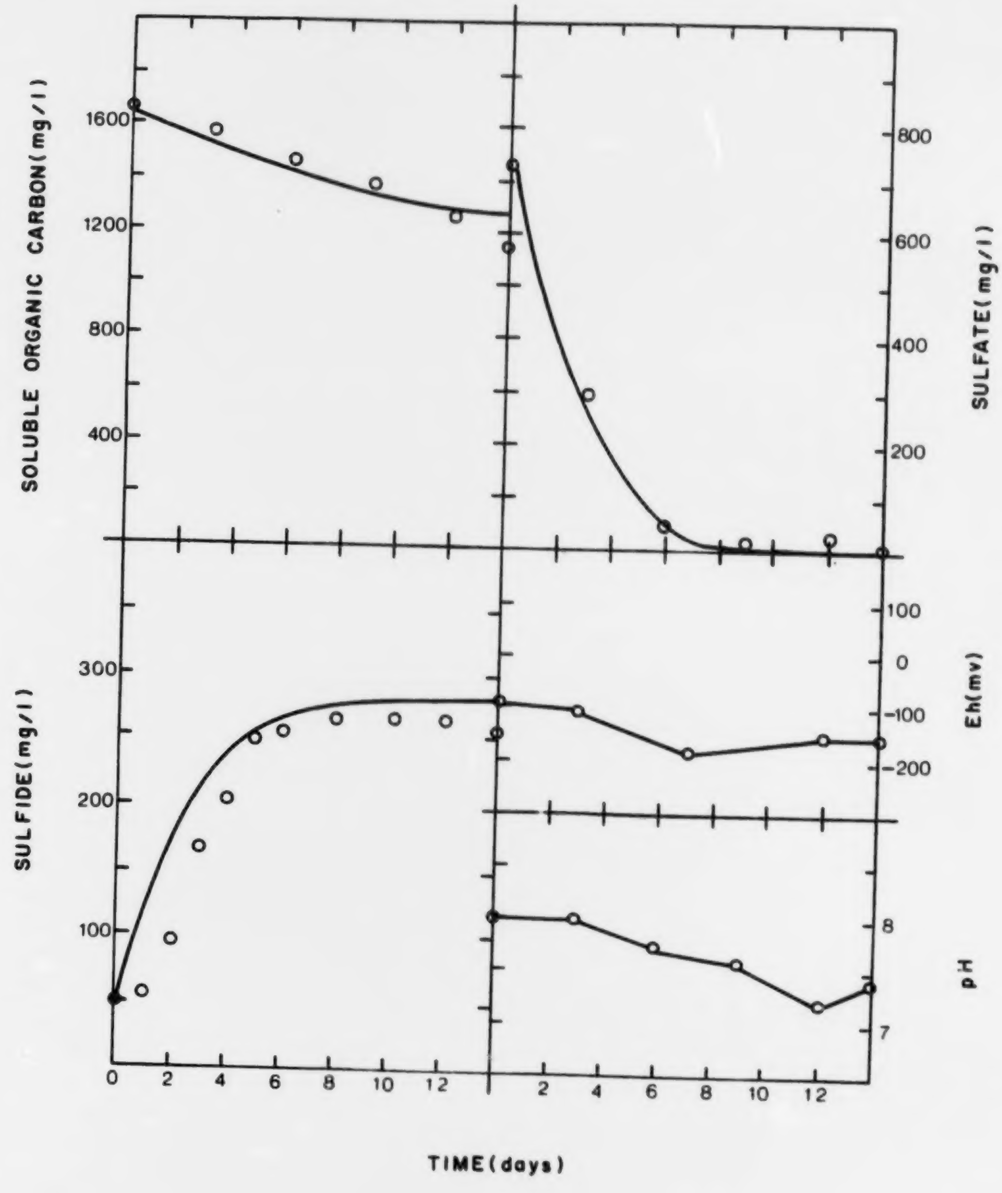


FIG. 16 - EXPERIMENTAL RESULTS OF CULTURE 4 COMPARED WITH EQUATIONS 23, 24, and 2

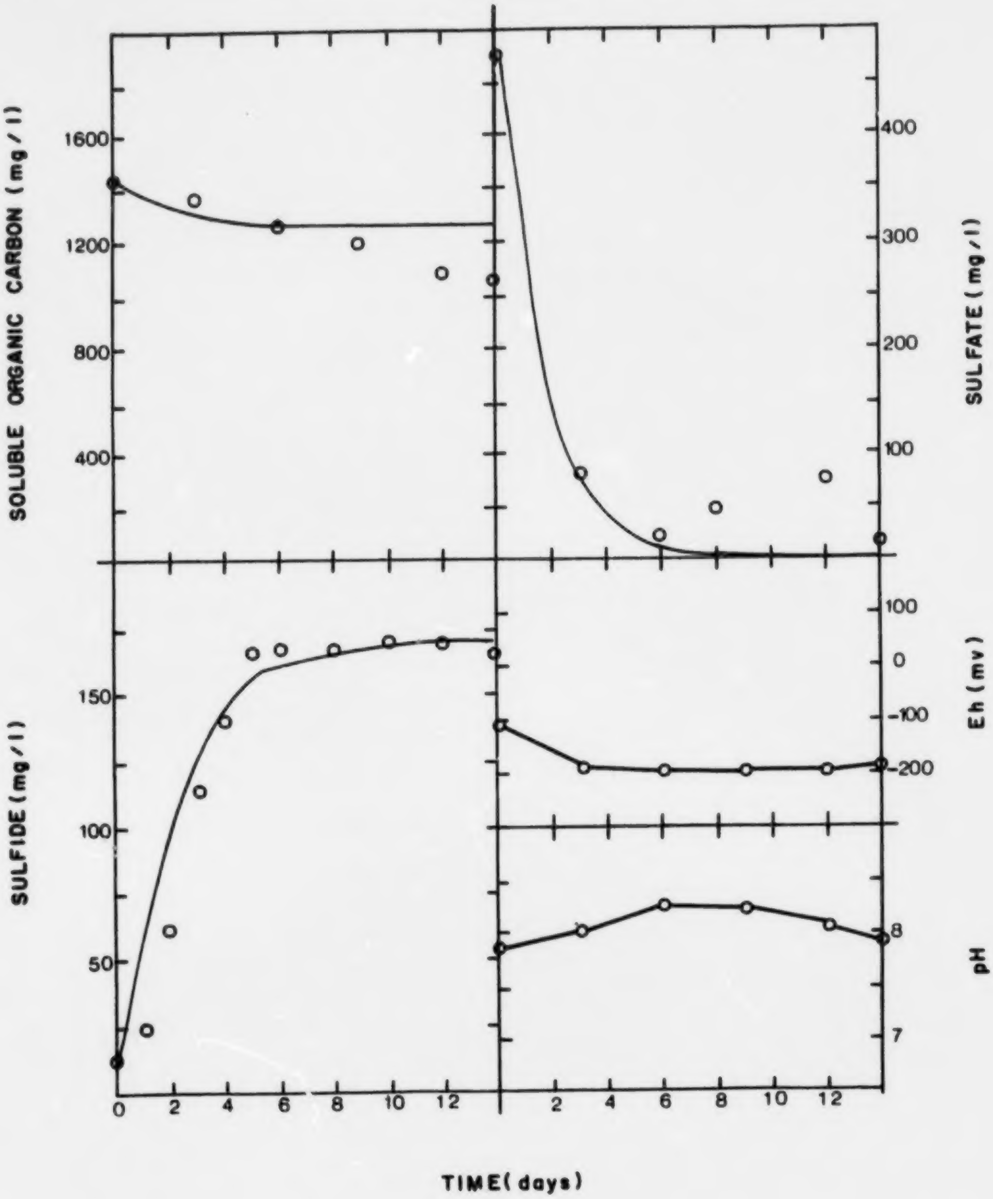


FIG. 17 - EXPERIMENTAL RESULTS OF CULTURE 5 COMPARED WITH EQUATIONS 23, 24, and 25.

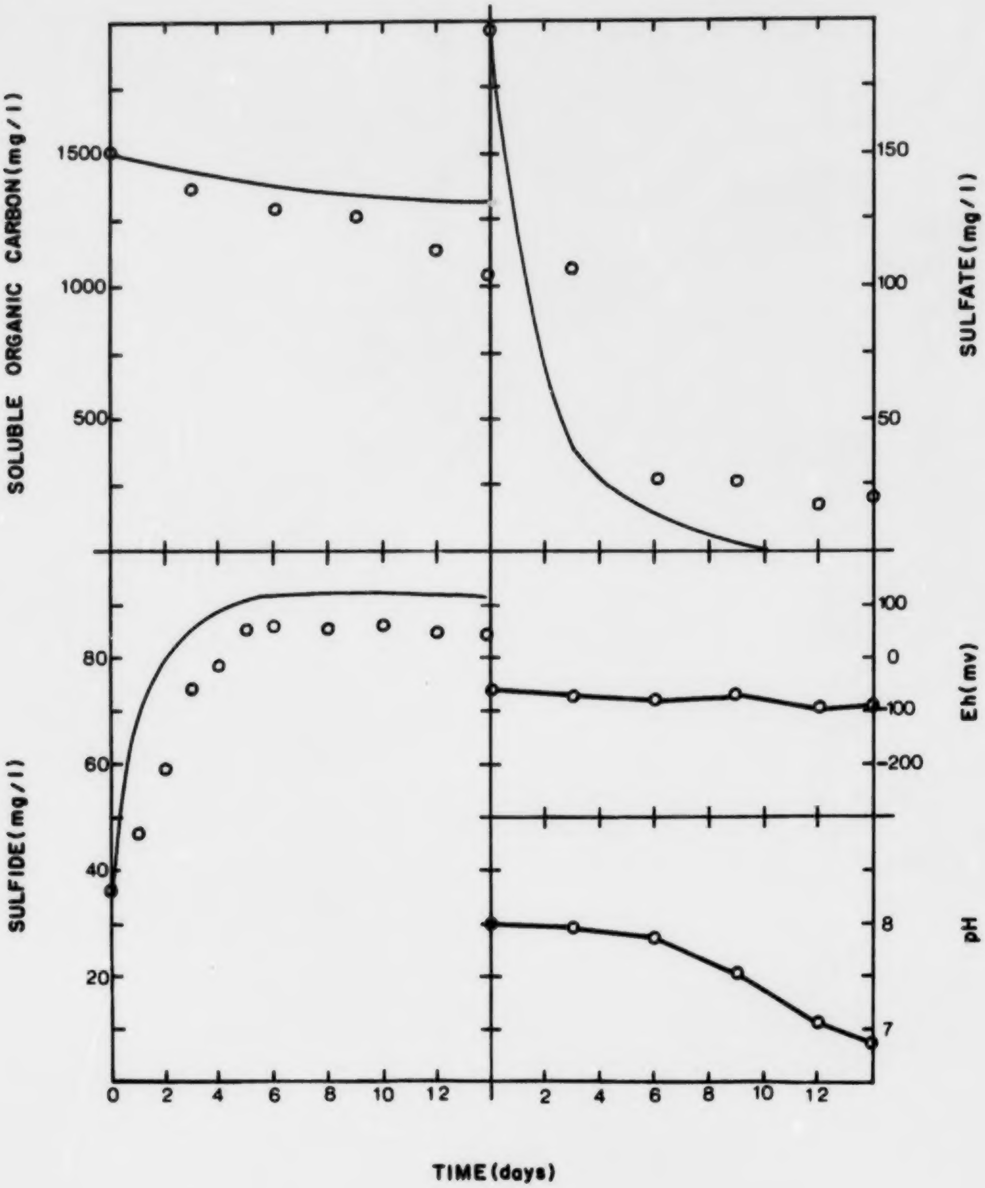


FIG. 18 - EXPERIMENTAL RESULTS OF CULTURE 6 COMPARED WITH EQUATIONS 23, 24, and 25.

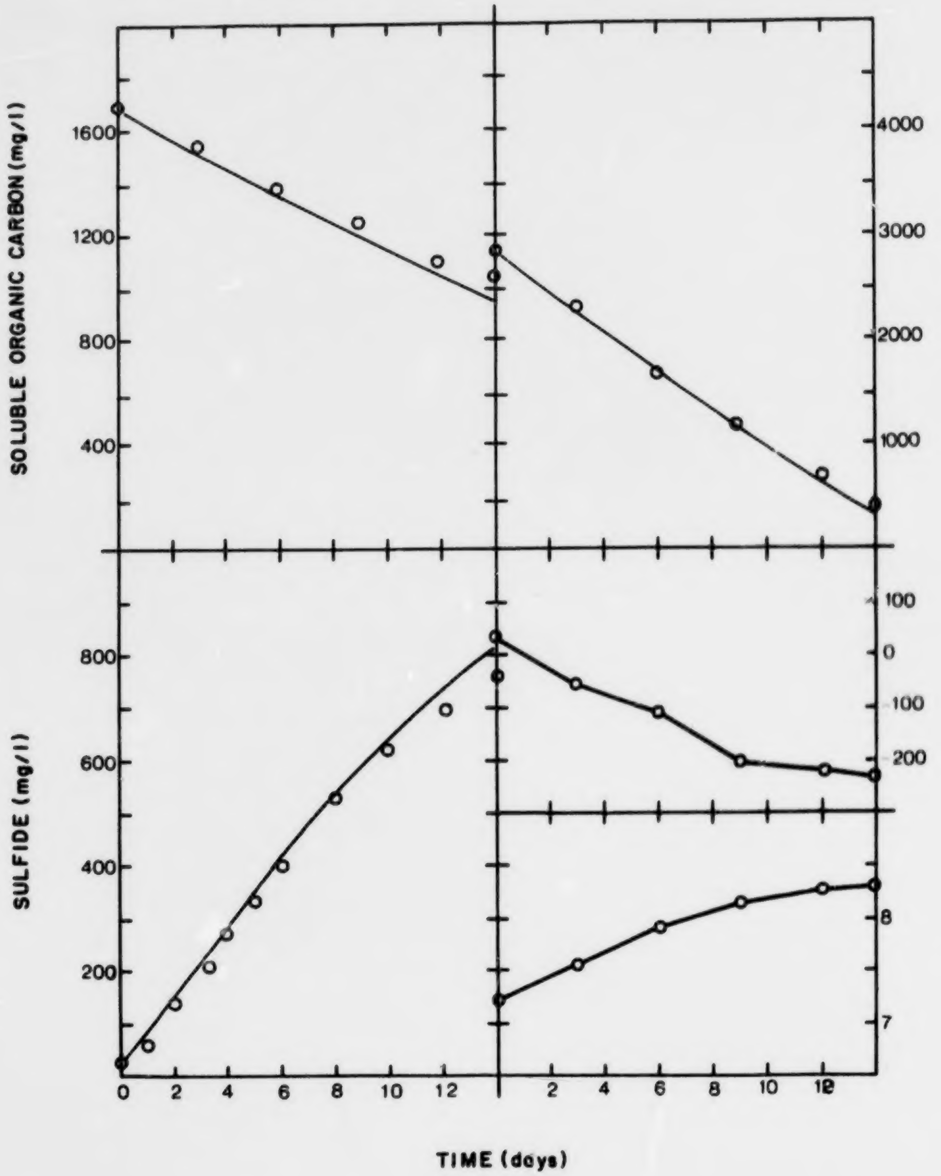


FIG. 19 - EXPERIMENTAL RESULTS OF CULTURE 7 COMPARED WITH EQUATIONS 23, 24, and 25.

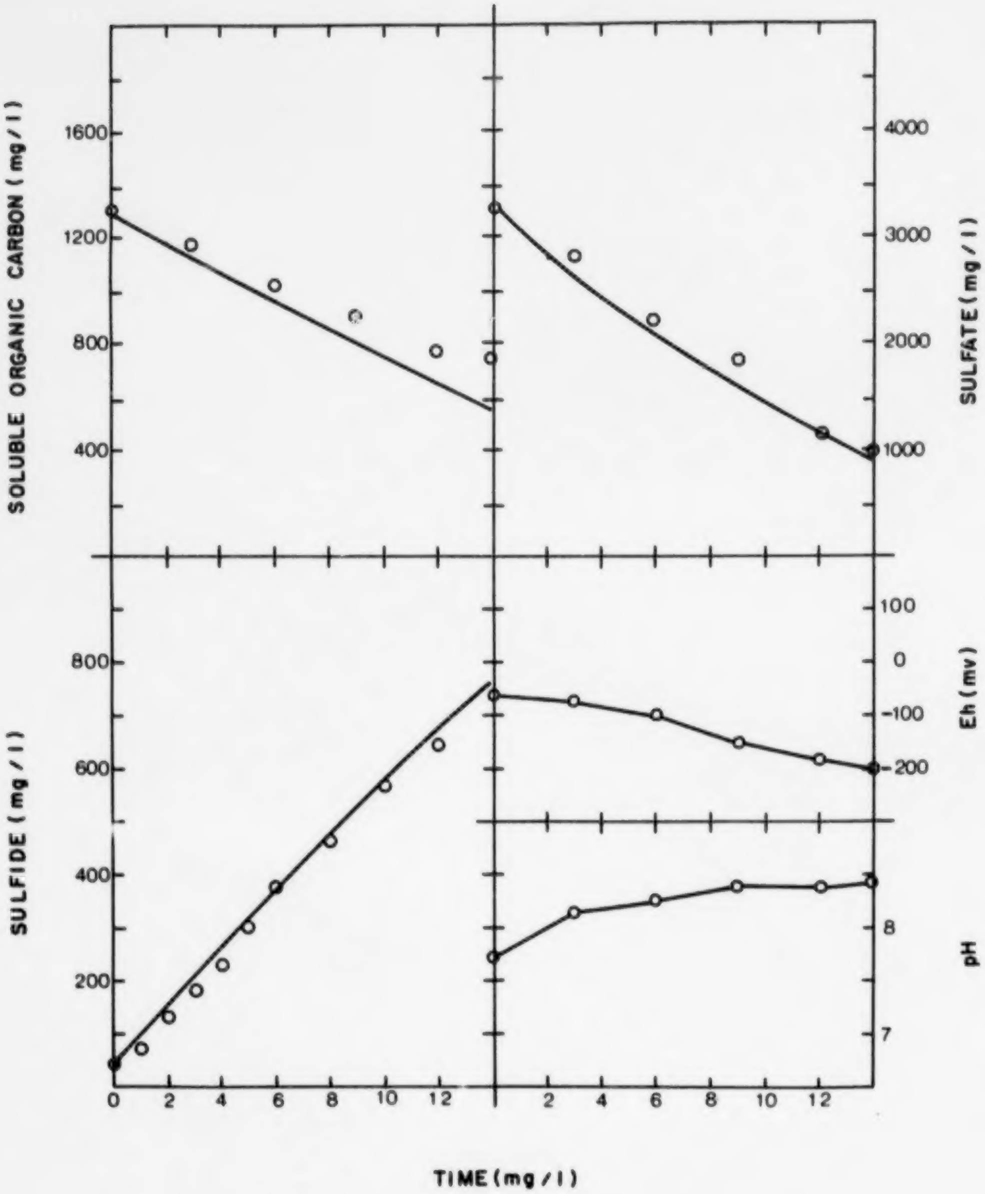


FIG. 20 - EXPERIMENTAL RESULTS OF CULTURE 8 COMPARED WITH EQUATIONS 23, 24, and 25.

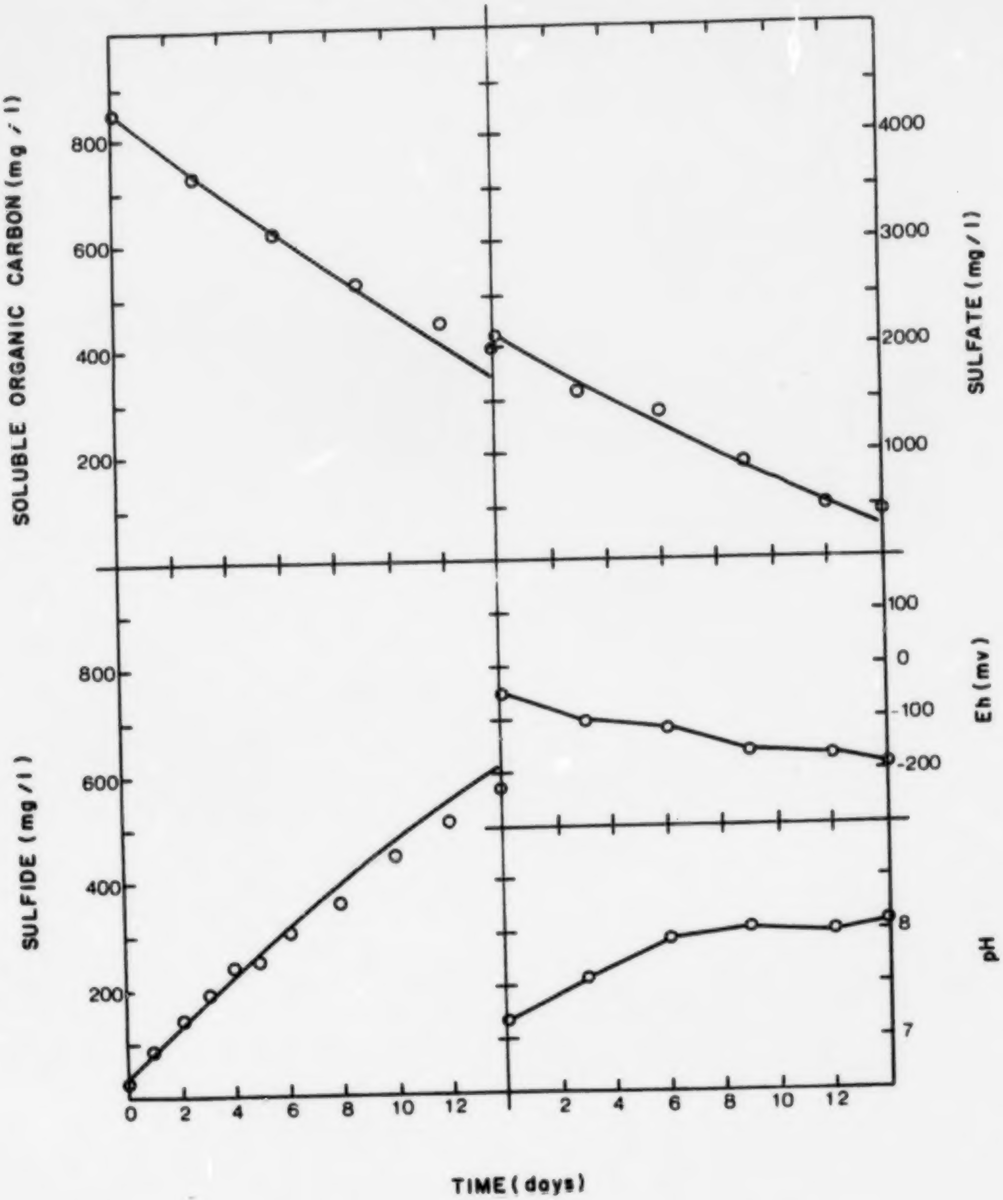


FIG. 21 - EXPERIMENTAL RESULTS OF CULTURE 9 COMPARED WITH EQUATIONS 23, 24, and 25.

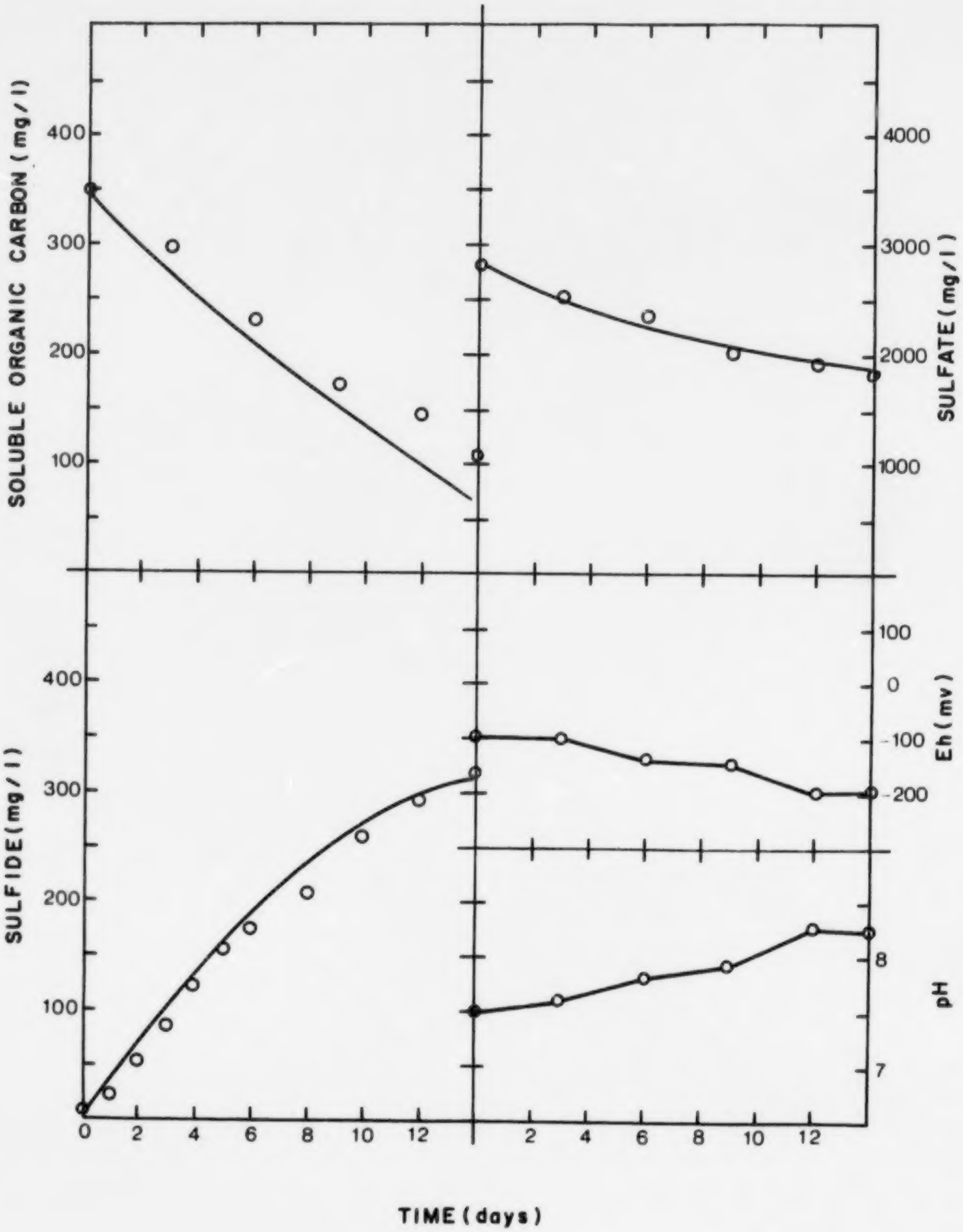


FIG. 22 - EXPERIMENTAL RESULTS OF CULTURE 10 COMPARED WITH EQUATIONS 23, 24, and 25

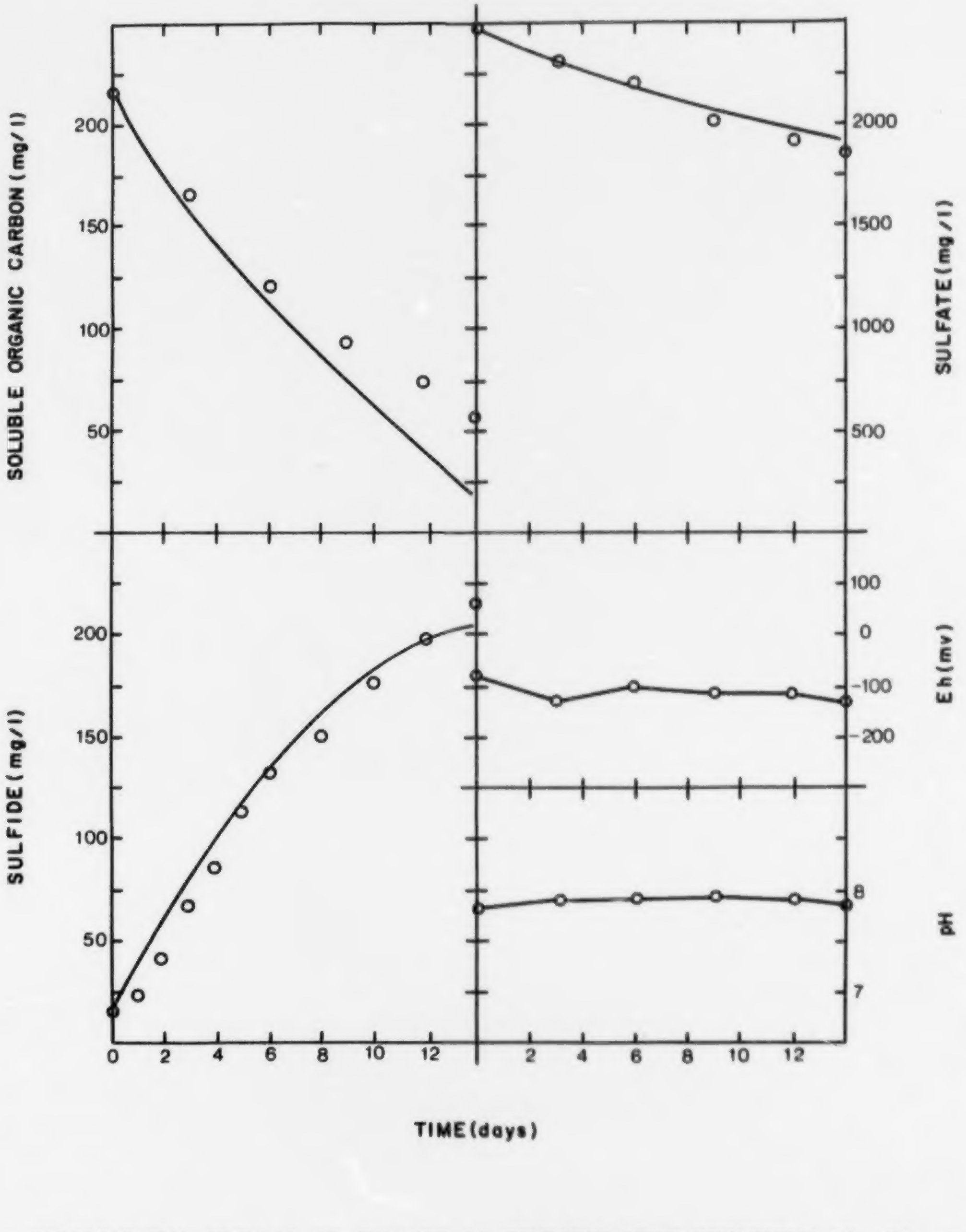


FIG. 23 - EXPERIMENTAL RESULTS OF CULTURE 11 COMPARED WITH EQUATIONS 23, 24, and 25.

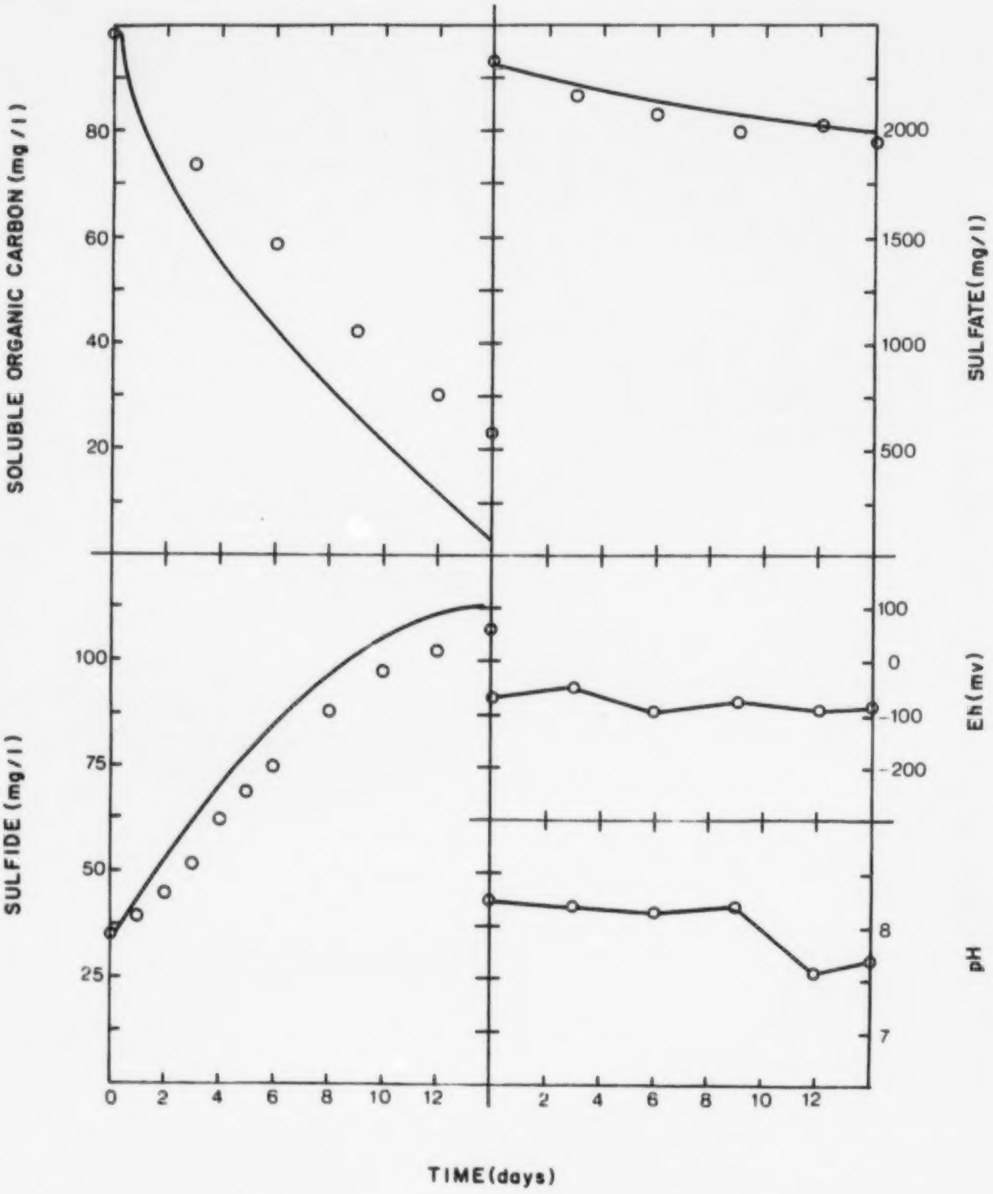


FIG. 24 - EXPERIMENTAL RESULTS OF CULTURE 12 COMPARED WITH EQUATIONS 23, 24, and 25

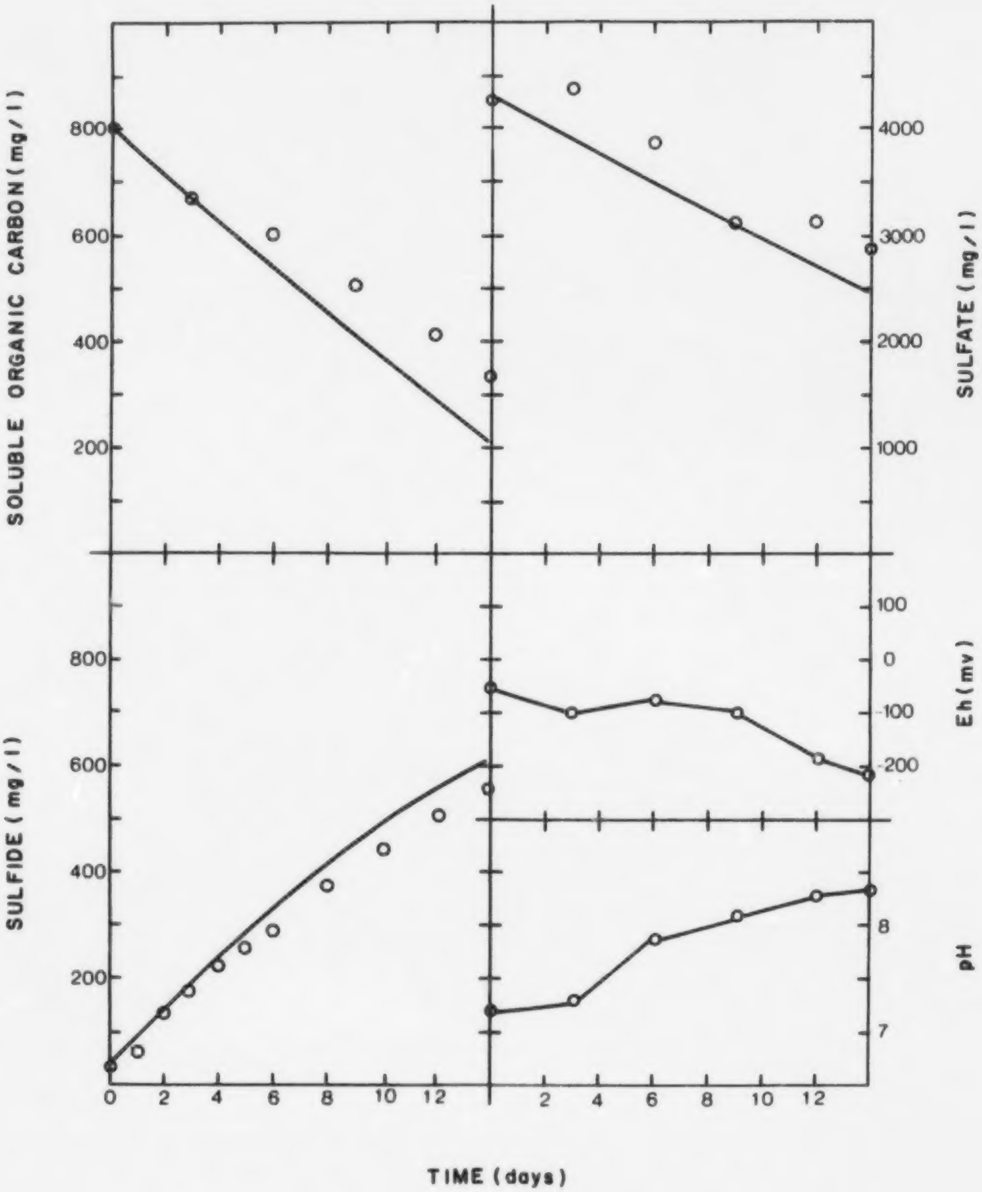


FIG. 25 - EXPERIMENTAL RESULTS OF CULTURE 13 COMPARED WITH EQUATIONS 23, 24, and 25.

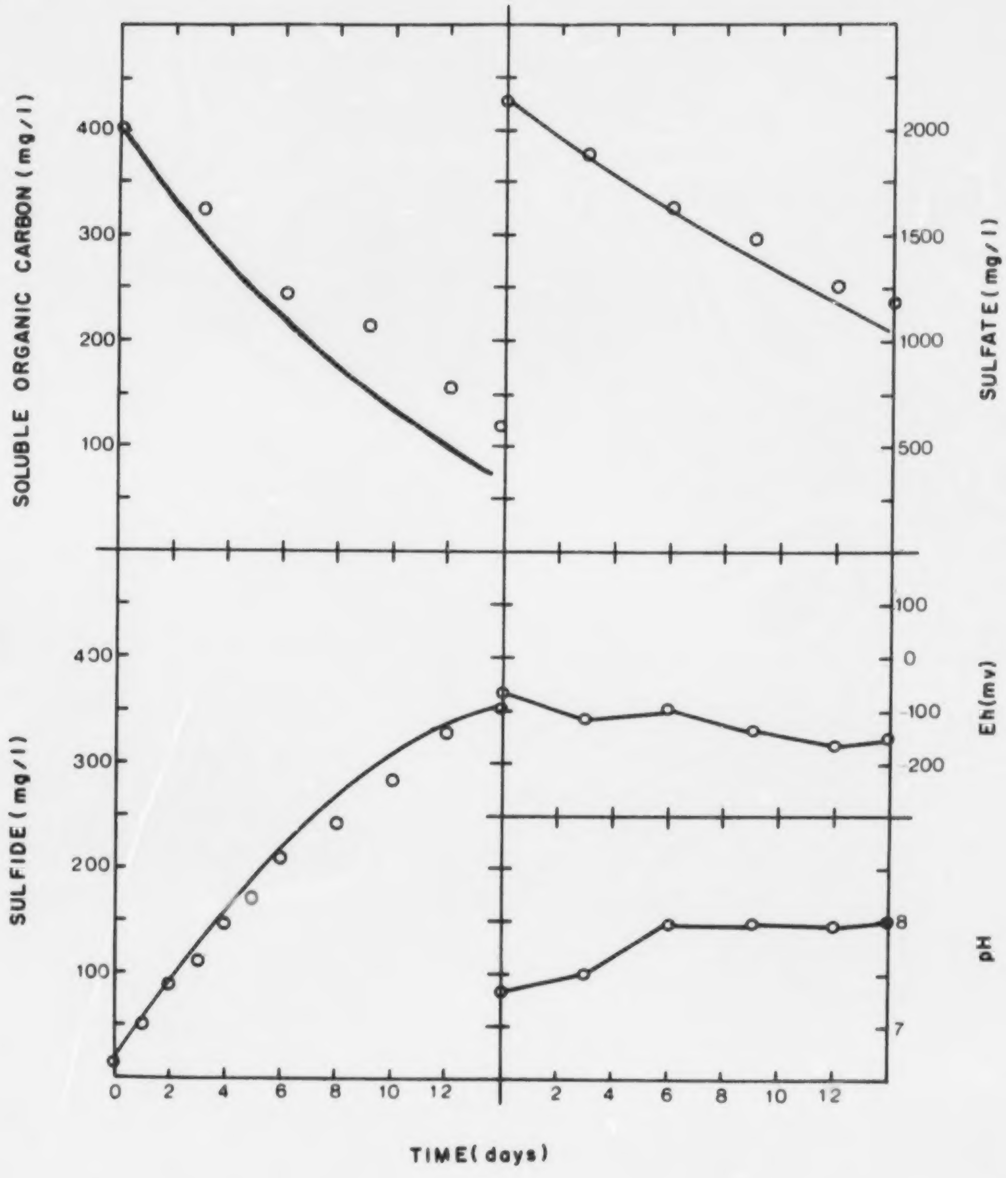


FIG. 26 - EXPERIMENTAL RESULTS OF CULTURE 14 COMPARED WITH EQUATIONS 23, 24, and 25.

SECTION X

SULFATE REDUCTION STUDY USING S-35

GENERAL APPROACH

In order to better quantify the extent of sulfate reduction that occurs within estuarine sediments a laboratory study employing S-35 was conducted (61). The study involved the placement of a known quantity of $Na_2S^{35}O_4$ into homogenized mud samples. Samples were then incubated. At selected time intervals, hydrogen sulfide was driven off as a gas and collected. The amount of S-35 within the collected sulfide was then determined. Thus, the percent of S-35 added as sulfate which was converted to sulfide over a given time interval could be calculated . With the known initial sulfate concentration of the sample, the rate of sulfate reduction could then be computed. Benthic samples were collected at site 5 with 2-inch I.D. plexiglas cylinders. Samples were transferred to the radiation laboratory at Corvallis, Oregon in a styrofoam cooler.

SAMPLE PREPARATION

Immediately after the samples had been taken to the laboratory, they were transferred to a portable plastic glove box containing a top loading single pan balance; a large glass trough; conical glass incubators, each of which has a side branch sealed with a tight-fitting rubber serum cap; and other necessary apparatus for sample transference. The glove box was then sealed and filled with pre-purified nitrogen which was being used to minimize excessive air entrainment into the soil samples during the transferring processes. The top 10 cm of the cores were extruded and homogenized in the glass trough.

Five (5) gm of the homogeneous soil sample and two (2) ml of glass-distilled water were carefully transferred into each tared incubator which was then stoppered and removed from the glove box.

Since biological sulfate reduction requires strict anaerobiosis, care was taken to remove all oxygen from the sample and the incubators used in the study. The gas in each stoppered incubator was replaced with pre-purified nitrogen by puncturing the rubber serum cap with a hypodermic needle connected to a glass manifold. This manifold consisted of 6 hypodermic needles, a three-wa valve, and a U-tube mercury manometer, and was connected through the 3-way valve to a vacuum line and to a supply of pre-purified nitrogen. The incubators were alternately evacuated and filled with purified nitrogen. During this process, a slightly reduced pressure was maintained in the incubators and the glass manifold, as was indicated by the mercury manometer. Using this procedure, intense reducing conditions were achieved in a relatively short period of time (15).

A known amount of radioactivity, approximately 1 microcurie, in the form of S-35 labeled sulfate solution ($Na_2S^{35}O_4$), was injected through the serum cap into the sample. The contents of each incubator were mixed by shaking vigorously for half an hour. The incubators were covered with aluminum foil to reduce excess growth of photosynthetic bacteria and algae, and were incubated at 18°C in a constant temperature room or water bath.

Cylindrical plexiglas vials of six inch long and four inch diameter were initially used for incubation. Because these vials leaked and many other difficulties were encountered during the addition of the radioactive sulfate solution, modified wide-mouth erlenmeyer flasks fitted with ground glass stoppers were used as incubators.

INITIAL CONDITIONS

The initial soluble sulfate concentration of the homogenized soil (prior to the addition of 2 mls distilled water to 5 gms of sediment) was determined by a colorimetric procedure using barium chloranilate (51). Approximately 30 gm of the soil sample were placed in an improved interstitial water sampler (50). Interstitial water was squeezed out when compressed at 80-100 psi and collected in a plastic hypodermic syringe. Then the water sample was filtered to remove most of the suspended matter. After filtration, the sample was passed through a Dowex 50 Wx-8 20-50 mesh H^+ cation exchange column to remove interferring ions. Ten ml of this extract was mixed with 2.4 ml of barium chloranilate solution and 1.6 ml of acetate buffer solution. The unused barium chloranilate and precipitated barium sulfate were filtered and 6.8 ml of the pink filtrate were mixed with 0.46 ml of EDTA - NaOH solution. The transmittance of the filtrate was determined at 520 mμ with a Beckman DB spectrophotometer. Sulfate concentration was read from a standard calibration curve.

The soluble organic carbon concentration in the interstitial water of the homogenized soil sample was determined. Five ml of the squeezed water were placed into a 20 ml screw cap test tube in an ice bath. Samples were tested in the Oregon State University Microbiology Department by using a Lira Infrared Analyzer Model 3000.

Water content of the homogenized soil sample was determined by drying the sample at 105°C.

COLLECTION OF SULFIDE

After incubation at 18°C for desired time periods, an incubator was removed from the constant temperature room, and carefully connected to the gas collection apparatus. The incubator was then lowered into a heated water bath. A small amount, several mg, of elemental mercury was added as a catalyst (62) into the sample before acid digestion.

The digesting agent, initially concentrated hydrochloric acid, was added into the incubator through a 250 ml pressurized separatory funnel connecting to a supply of pre-purified nitrogen used as a carrier gas for evolved hydrogen sulfide. Concentrated hydrochloric acid was later substituted by hydriodic acid because concentrated hydrochloric acid was found to react very slowly with several mineral sulfides, such as pyrite and chalcopyrite (63).

The released hydrogen sulfide was carried by a stream of pre-purified nitrogen through a train of gas wash bottles, each of which contained 100 ml of 5N sodium hydroxide solution. The gases being emitted from the sampling train were tested for any trace of hydrogen sulfide by using lead acetate solution or a Kitagawa low concentration hydrogen sulfide detection tube. After the complete decomposition of the soil sample, the apparatus was continuously purged with pre-purified nitrogen for about an hour.

After acid digestion and the purging of the soil sample with nitrogen, the pressure within each gas wash gottle was released by venting to the atmosphere through the 3-way valves connected between the three gas wash bottles. The valves were turned off in a reverse sequence; that is, the pressure in gas bottle 2 was released before that of the first. Then the nitrogen supply was turned off.

One ml of the sodium hydroxide-sodium sulfide mixture in each wash bottle was injected into a liquid scintillation counter vial containing 18 ml of "Aquasol" and 2 ml of distilled water. The activity of the sodium hydroxide-sodium sulfide mixture was measured by a Tri-Carb Scintillation Counter with a photomultiplier voltage gain of 12.2% and window settings of 40 and 1000 respectively.

During the acid digestion process, condensate was formed and accumulated in the connection between the incubator and the first gas wash bottle. A large Y-connector had been used to join the incubator and the gas wash bottle. The sample of the condensate was injected into a liquid scintillation counting vial containing 20 ml of Aquasol. The condensate was found to contain some radioactivity. Thus, not all of the S-35 released as hydrogen sulfide was collected in the gas collection bottles. It was felt that this amount was quite small, however, future studies should account for the amount.

It was observed that there was a possibility of contamination of the sodium hydroxide solution in the first gas bottle. Therefore, it was decided that any succeeding studies would employ a condenser connected at the top of the incubator so that only relatively dried and cooled gases could pass into the gas wash bottles.

Radioactive tracer assays, based on the liquid scintillation counting method, depend on the optimization of the counting efficiency, which is mainly influenced by two main factors:

(1) The figure of merit (64).

(2) The counting efficiency of the counter for S-35 isotope.

The figure of merit, (S^2/B) is the highest possible counting rate of the specific isotope and the lowest possible counting rate of the background. It was determined by continuous measurement of the net count rate of the activity of a known standard S-35 solution(S) and of the background (B) while periodically altering voltage gain of the photomultiplier. The optimum condition was achieved when the voltage gain setting established a maximum value for the expression S^2/B.

In order to determine the efficiency of the counter for the activity of S-35 isotope, the quenching effect had to be considered. The quenching effect is any reduction of efficiency in the energy transfer process in a given liquid scintillation counting sample, said reduction being caused by color quenchers, chemical quenchers, and diluters. For the Tri-Carb Scintillation counter, the quenching effect for each sample is determined by an external standard, and the result is expressed as Automatic External Standard (AES) Ratio (64).

The counting efficiency, the ratio of the net photon count rate in cpm to the disintegration rate (decay rate) in dpm, associated with each quenching condition was determined by adding variable amounts of chloroform, a chemical quencher, to a series of samples containing 20 ml of Aquasol and a known amount of radioactivity of S-35 (65). A quenching calibration curve of the AES ratio versus the percentage counting efficiency was plotted.

For each sample that was used in the study of microbial sulfate reduction, the disintegration rate was determined with the quenching calibration curve and an average value of the net count rate. The disintegration rate was then converted to radioactivity in micro-curies by dividing the dpm value with 2.22×10^6. Since S-35 isotope has a half life of 87 days, the experimentally determined radioactivity had to be corrected using the equation for self disintegration:

$$N = N_o e^{\mu\tau} \tag{26}$$

where N = the measured activity in μc
N_o = the actual activity in μc if no self disintegration exists

λ = decay constant = 0.00794/day

τ = time in days since the addition of S-35 activity to the soil sample.

The total amount of labeled sulfide generated microbially was determined by multiplying the summation of the total actual activity by the total volume of sodium hydroxide solution used to capture the hydrogen sulfide gas.

RATES OF SULFATE REDUCTION

The results of two concurrent experiments are summarized in Table 10. The results show that sulfate reduction proceeded without a significant lag time. The maximum rate of sulfate reduction was approximately 71 mg of sulfide ($S^=$) produced per day per liter of interstitial water of the original sample. Recall, however, that 2 mls of distilled water were added to 5 gms of wet sediment. Within this mixed slurry, the maximum rate would be approximately 46 mg/L-day. These results are remarkably close to the results obtained from the extract experiments previously described. If a lag time did occur within the first three day period, however, the maximum rate would have been higher.

The results indicate that the experiments were approaching ninety percent recovery of the original S-35. The apparent lack of total recovery with time may have been due to the experimental proceedure. As explained, S-35 did collect in the lines to the gas collection flasks. Physical adsorption and biological incorporation may also have resulted in a delay in the release of the remaining ten percent as hydrogen sulfide.

In addition to maximum rates of sulfate reduction comparable to the extract experiments, the S-35 experiments also suggest that the rate of sulfate reduction does not become sharply limited by the sulfate concentration until sulfate concentrations fall below 200-300 mg/L. This observation is in agreement with the results of the extract experiments previously described.

TABLE 10. SUMMARY OF S-35 RECOVERY

Incubation Time (days)	Recovered S-35 (percent)	
	Run 1	Run 2
3	37.86	40.98
6	70.02	68.46
9	77.8	76.24
14	79.36	80.39
21	85.06	83.5
28	85.29	83.71

Study conducted during summer 1971.

SECTION XI

OTHER ESTIMATES OF SULFATE REDUCTION

DIFFUSION OF SULFATE

It is possible to obtain an estimate of the rate of sulfate reduction within a deposit by considering the downward flux of SO_4. If the deposit has remained undisturbed for a sufficient time, a steady state will be approached which may be approximated by the equation

$$D_L \frac{\partial^2 L}{\partial z^2} = A \tag{27}$$

in which D_L is the diffusion coefficient for sulfate (assumed to be constant with depth), L is the sulfate concentration, z is the depth from the sediment surface and A is the mass of sulfate removed per unit time per unit volume of interstitial water. Assume that A is constant with depth until L becomes limiting at concentration L'. Below the limiting depth (the depth at which L=L'), A will be equal to zero. The following equation is then obtained from equation (27)

$$A = \frac{2D_L(L_o - L')}{z'^2} \tag{28}$$

in which L_o is the concentration of sulfate of the sediment surface and z' is the limiting depth at which L=L'. The maximum value of L_o will be 2655 mg/L (the sulfate concentration in sea water). The solution of equation (28) for values which might be common with estuarine sediments is graphically shown in Fig. 27. A reasonable (9) value for D_L(.5 x 10^{-5} cm^2/sec) is shown within a range ($10^{-6} cm^2$/sec to 10^{-5} cm^2/sec) that might be expected.

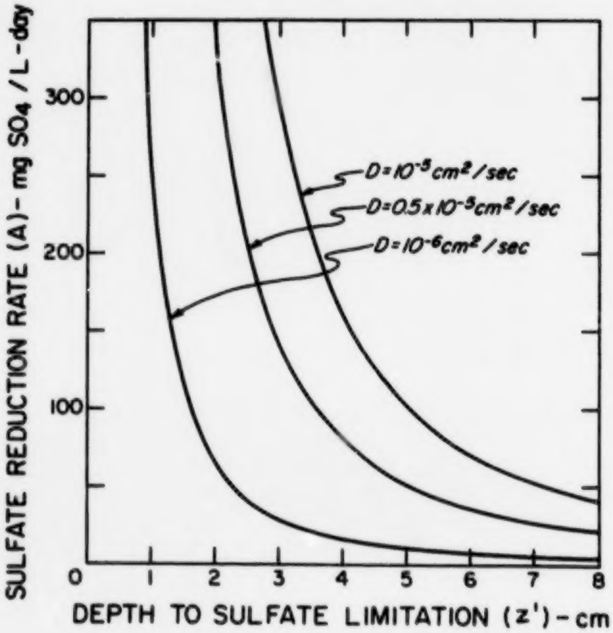


FIG. 27 - RELATIONSHIP OF SULFATE REDUCTION RATE TO SULFATE DIFFUSION ASSUMING STEADY S

A number of sulfate profiles within the sediments of tidal flat areas were measured and more than twenty such profiles were obtained. Most did not appear to be approaching the steady state described above. That is, the variation of L with depth similar to the solution of equation (27) was not clearly defined. For most profiles, scour and partial turnover appeared to have influenced sulfate profiles. The profile shown in Fig. 10 does indicate an z' value of approximately 3 cm. It is difficult to define the sulfate profile within a depth of 3 cm. Moreover, the uneveness of the mud surface, the looseness of the deposit surface and the influence of partial scour should be recognized. Thus the use of equation (28) can only be expected to provide an order of magnitude estimate of A. Using the values, $z'=3$ cm, L_o-L' = 1500 mg/L and $D_L = 0.5\text{x}10^{-5}$ cm^2/sec, one obtains an approximate value of A equal to 150 mg/L-day. This corresponds to a rate of sulfide production of 50 mg/L-day (as S) which falls within the range of the experimental results previously discussed.

INCUBATION OF BENTHIC CORES

Estimates of the rate of sulfate reduction were obtained by collecting a number of sediment cores at a given site in 2 inch I.D. plexiglass tubing. Cores were incubated at room temperature (approximately 25°C) and profiles of sulfate concentrations within the interstitial water of cores were determined at time intervals of 1 to 6 days. Rates of sulfate reduction were calculated by determining the differences of sulfate concentrations between cores incubated for different time periods. No corrections for the diffusion of sulfate were made. Effort was made to collect cores from areas where the deposits appeared to be horizontally uniform. Variations between cores from which the rates were determined, however, did result in considerable scatter of results. A summary of the rates so determined are given in Table 11.

TABLE 11. SULFATE REDUCTION IN CORES AT ROOM TEMPERATURE (25 °C)

Starting Date	Site	Sediment Temp. (°C)	Volatile Solid (%-dry weight)	Initial SO_4 (mg/1)	SO_4 Reduction (mg/1-day)	S Production (mg/1-day)
10/ 1/71 (a)(b)	4	--	13-16	1000	50	17
10/18/71 (a)	4	13	---	1100	40	13
10/18/71 (a)	4	13	---	700	30	10
10/ 2/71 (c)	5	18	13-20	1000	100	33
10/ 7/71 (c)(d)	5	15	15	800	70	23

(a) Values averaged over top 4 cm of core

(b) Soluble organic carbon = 15-130 mg/1

(c) Values averaged over top 3 cm of core

(d) Soluble organic carbon = 33-215 mg/1

SUMMARY OF SULFATE REDUCTION RATES

The rates of sulfate reduction measured during this study are compared to those reported by other investigators (Table 12). Maximum rates in the study by Edwards (60) were higher than those measured in this study. The higher incubation temperature (30°C), and use of sufficient lactate (a completely utilizable carbon source) to produce soluble organic concentrations above those in the extract's media (Section IX) would likely account for these higher rates. The maximum rates measured by Nakai and Jensen (66) were within the range of those reported measured in this study. Measurements by Ivanov (20) and Sorokin (21) of sulfate reduction in lake muds were determined through the use of labeled sodium sulfate ($NA_2S^{35}O_4$). The difference in units used to report their rates makes comparison difficult. If it is assumed that their mud samples were roughly 50 to 75 percent water, then the reported rates would range up to approximately 40 mg sulfide per liter per day. In their study, 10 cm mud samples were utilized and the rates reported based on production of sulfide over this depth. If the production were occurring within only the top few cm, however, then the rates reported might underestimate the actual production occurring within this active upper region. Accounting for these factors would produce approximate agreement with the range of those measured in this study. None of the studies shown in Table 12 provide estimates of the rate of sulfate reduction that might occur immediately below the mud surface. Within the upper anaerobic regions of high organic deposits, rates higher than those shown in Table 12 might be possible particularly within the regions immediately under dense algal mats.

TABLE 12. COMPARISON OF THE RATES OF SULFIDE PRODUCTION MEASURED IN THIS STUDY WITH THOSE OF PREVIOUS INVESTIGATORS

Investigator	Sulfide Production rates (a)	Comments
This study	10-70 (b)	Sediment Extracts, See Section IX
This study	46 (b) (c)	Mud Slurry, See Section X
This study	50 (b)	*In situ* sulfate profiles, order of magnitude only, see Section XI
This study	10-23 (b)	Incubation of cores, limited study, see Section XI
Edwards (65)	200-250 (b)	In lab, pure batch cultures of D. desulfuricans on Macpherson's medium, stable populations
Edwards (65)	100-150 (b)	In lab, pure batch cultures of D. desulfuricans on Macpherson's medium, stable populations
Ivanov (20)	0.5-1.5 (d)	Field measurements in 10 cm mud cores from deepest part of lake, determined with S^{35}
Ivanov (20)	12-19 (d)	Field measurements in 10 cm mud cores from slope of lake, determined with S^{35}
Nakai and Jensen (66)	10-45 (b)	In lab, mixed cultures containing sulfate reducing bacteria, cultures consisted of 30 ml sea water and 65 ml wet sediment
Sorokin (21)	0.1-0.2 (b)	Field measurements in lake water using S^{35}
Sorokin (21)	10-15 (d)	Field measurements in muds collected from slope of lake near river mouth, S^{35} used

(a) Approximate range

(b) mg(S)/1- day

(c) Maximum rate

(d) mg(S)/ Kg wet sediment-day

SECTION XII

BENTHIC SULFIDE RELEASE

GENERAL

Attempts were made to measure the benthic sulfide release at site 5 through the use of a benthic respirometer. A single successful respirometer run was completed during the summer of 1970. A sulfide release rate of 1.6 gm gm/m^2-day was measured in a 2-1/2 hour run without correction for oxidation of free sulfide. An oxygen depletion rate of 3.2 gm/m^2-day was also measured. If approximately half of this oxygen uptake rate was due to the oxidation of free sulfides, then the total sulfide release rate may have approached 3.2 gm/m^2-day. The respirometer was later modified to permit nitrogen gas sparging of DO from the installed respirometer. Three additional respirometer runs were repeated at site 5 during the summer of 1971. (67)

MODIFIED BENTHIC RESPIROMETER

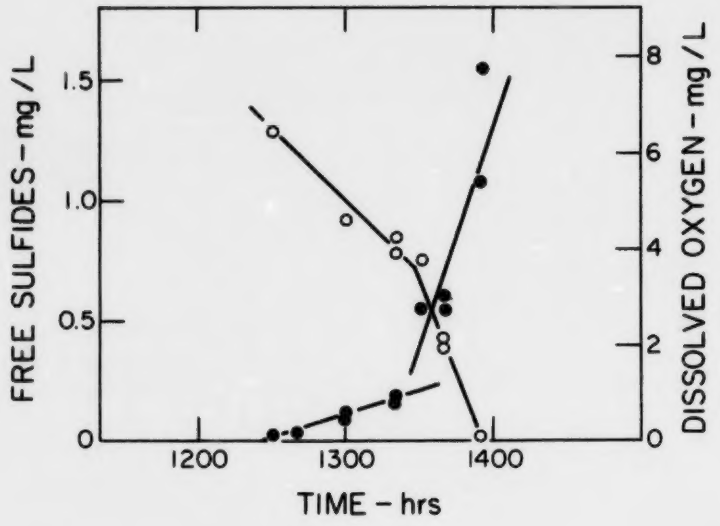
The modified benthal respirometer (similar to that described in Section VI) consisted of a black plexiglas tunnel, a small submersible pump, an expansion chamber, a system of hoses, a flow indicator, a sampling port, and a sparging unit. The tunnel was 2-7/8 inches in diameter, 49 inches long, with 2-inch flanges attached to the base, and covered an area of 282 square inches (0.182 square meters). It was painted black to prevent photosynthetic oxygen generation by algae covering the benthal deposit. The tunnel was placed on the mud at low tide and filled by the rising tide through holes in the top which are then sealed by rubber stoppers. Water was circulated at a rate of about 4 gallons per minute through the device in order to thoroughly mix the contents and facilitate sampling at the estuary's water surface. Water was circulated through a 5/8-inch diameter garden hose. A strip of plastic cloth was installed to flutter inside a three-inch length of clear plastic tubing to indicate that flow was being maintained. Sampling was done with a 30 ml syringe through a septum installed in a plastic "tee" located on the circulation hose. Duplicate samples were taken every twenty minutes for DO and free sulfide measurement by methods described in the previous section.

At the onset of the 1971 runs, nitrogen gas was sparged into the pressure line of the pump, collected in the expansion chamber, and relieved through a valve in that chamber. This chamber, made from a 27-liter plastic carboy, had inlet and outlet fittings and an adjustable relief valve. Nitrogen sparging was intended to strip the DO from the water, and thus permit the buildup of free sulfides without oxidation.

Care had to be used during sparging to maintain the same volume of water within the device by adjusting the release rate to equal the sparging rate. Constant volume was necessary to facilitate computation of the mass of sulfide released from the observed rise of sulfide concentration. This was done with the aid of a line on the expansion chamber to indicate a constant gas volume. The total volume of water within the device, with one liter of gas in the expansion chamber, was 38 liters. Excess pressure had to be avoided to prevent pushing the tunnel off the mud, as happened in the earlier runs.

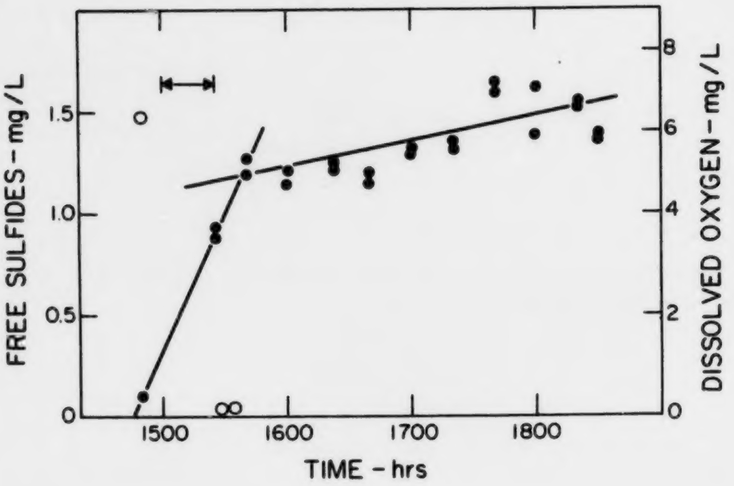
RESULTS OF SULFIDE RELEASE MEASUREMENTS

The results of the 1971 runs are presented in Figs. 28, 29 and 30. The release rate of sulfide in each experiment was expressed by a high and low rate shown by the lines in these figures and in Table 13. When DO was present, the sulfide release rate increased with time. When nitrogen sparging removed the DO, the sulfide release rate decreased with time. A number of explanations



● = free sulfide
o = dissolved oxygen

FIG. 28 - BENTHIC SULFIDE RELEASE WITHIN RESPIROMETER - SITE 5 - 8/3/71.



● = free sulfide
o = dissolved oxygen

FIG. 29 - BENTHIC SULFIDE RELEASE WITHIN RESPIROMETER - SITE 5 - 8/9/71. (Period of Nitrogen sparging shown by arrow).

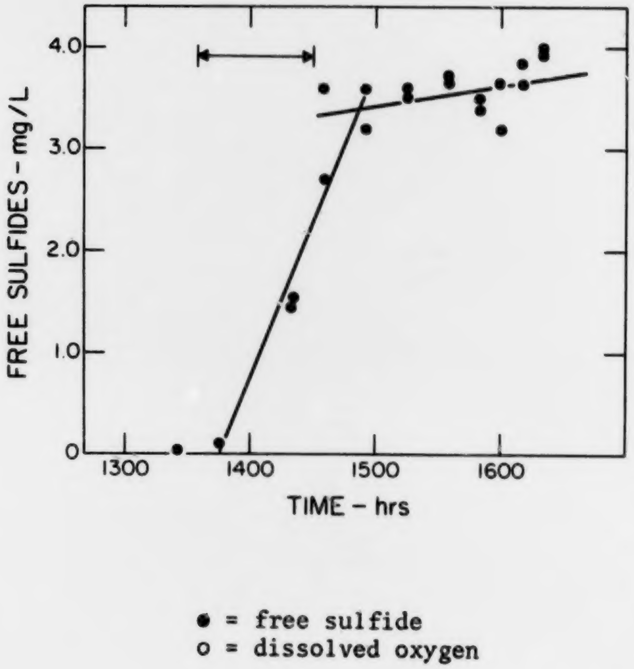


FIG. 30 - BENTHIC SULFIDE RELEASE WITHIN RESPIROMETER - SITE 5 - 8/20/71. (Period of Nitrogen sparging shown by arrow.

TABLE 13. ESTIMATES OF SULFIDE RELEASE RATES AND OXYGEN UPTAKE RATES AS MEASURED IN RESPIROMETER EXPERIMENTS AT SITE 5

Date	S Release Rate (gm/m^2-day)	DO Uptake Rate (gm/m^2-day)
9/ 3/70	1.6- 3.2(a)	3.2
9/ 3/71	1.0- 9.2	-
9/19/71	0.8- 7.2	15-39(b)
9/20/71	1.0-15.0	-

(a) Upper estimate based on assumption one half DO uptake due to sulfide oxidation with one to one sulfide oxygen mass ratio.

(b) High rates may be due to interference of DO measurements.

are possible and the data are not adequate to select from such explanations. The initially high rate during the 8/9/71 and 8/20/71 runs may have resulted from the disturbance of the bottom by the respirometer. In these same runs, the decline in the sulfide release rate may have resulted from the input of Fe^{++} and the formation of FeS. The termination of nitrogen sparging may also have contributed to the decline in sulfide release. The high DO decrease in the 8/3/71 run may be due to sulfide interference of the micro-winkler test.

The difficulties in performing these respirometer runs should not be underestimated and the results must be interpreted with these difficulties in mind. The results including the 1970 run do indicate that the sulfide release rate in this region during late summer likely falls in the approximate range of 1.0 to 10.0 mg $S^=/m^2$-day. Any finer evaluation of the results is likely unwarranted. More reliable sulfide release rates would likely be obtained through the use of laboratory flow-through systems. The benthic sulfide release rates which are possible within a range of measured sulfate reduction rates are shown in Table 14. These rates are maximum values as it is assumed that all sulfide produced is released.

PROFILES OF FREE SULFIDE

Free sulfide concentrations were measured within the interstitial waters of sediment cores. In general, gradients of free sulfides seldom exceeded 40-50 mg/l-cm (see Fig. 11) and this value was approached only at site 5. If the release of free sulfides depended on molecular diffusion only, such gradients would result in a sulfide release rate of approximately 0.2 gm/m^2-day. Maximum free sulfide gradients within the immediate surface regions of the deposits, however, were likely higher than those measured due to the difficulty of sampling interstitial waters within small distances. Moreover, partial turnover of the immediate surface regions can be expected and thus the upward flux of free sulfide would be increased. Thus the value of 0.2 gm/m^2-day is likely a low estimate of the higher benthic sulfide release rates attained at site 5.

SUMMARY OF BENTHIC SULFIDE RELEASE EXPERIMENTS

Measurement of benthic sulfide release likely occurred for any prolonged period only at site 5. This site had all of the conditions which would contribut to maximum sulfide releases. Experimental results were extremely variable and one can only conclude that sulfide release rates approximating 1.0 gm/m^2-day should not be considered unreasonable for conditions similar to those of site 5. This estimate is extremely crude, however, given the very limited and variable experimental results. Moreover, site 5 is not typical of estuarine tidal flats and the average sulfide release rates for typical tidal flats can be expected to be considerably lower than those experienced at site 5.

TABLE 14. POTENTIAL BENTHIC SULFIDE RELEASE RATES (GMS/M^2-DAY) (a)(b)

Average Rate of S Production mg/l-day	Depth of Sulfate Reduction-cm				
	2	3	4	5	6
20	0.2	0.3	0.4	0.5	0.6
40	0.4	0.6	0.8	1.0	1.2
60	0.6	0.9	1.2	1.5	1.8
80	0.8	1.2	1.6	2.0	2.4
100	1.0	1.5	2.0	2.5	3.0

(a) Assume 50% water content by volume

(b) Assume all sulfide produced is released

SECTION XIII

MIXING WITHIN DEPOSITS

GENERAL

The vertical mixing that occurs within estuarine benthic systems is an important factor in determining the conditions within the benthic system and the influences of the benthic systems upon the overlying water and air. Vertical mixing within deposits depends on a variety of factors. Hydraulic factors, such as tidal changes in water depth, water velocities, wave action and low tide drainage patterns all contribute toward vertical mixing (68)(69). The burrowing and movement of organisms within deposits leads to greater vertical mixing (38)(70)(71). Dye tests at site 2 indicated a large exchange of water through mud-shrimp burrows (34). The presence of fine particles within the deposits tends to reduce vertical mixing (68)(69). Ebbing waters were found to drain freely through the deposits at site 1 while a lack of such drainage was noted at station 5. Water velocities measured at sites 3 and 4 with a price current meter were generally below 0.6 fps.

The presence of biological growth may retard the passage of water through the deposits and thus reduce the hydraulic tidal mixing. At site 1, permeabilities of 0.04-0.03 cm/min were measured at locations where biological growths were not noted while, in this same general region, the permeability in the top twelve centimeters was reduced to 0.0008 cm/min in areas of noticeable biological growth on the deposit surface.

In regions where vertical mixing is reduced to that of molecular diffusion, the departure from straight-line diffusion, due to the deposit particles, reduces molecular diffusion coefficients by approximately 30 percent from that of pure water (72)(73). Electric interaction between particles and interstitial water can also lead to a reduction of molecular diffusion (74). Diffusion within biological slimes can also be significantly less than diffusion through pure water (75). Vertical mixing can thus be expected to vary from relatively large hydraulic exchanges, often facilitated by burrowing organisms and large particle sizes (site 1), to values less than that of molecular diffusion in pure water. Vertical mixing can thus be expected to vary from relatively large hydraulic exchanges, often facilitated by burrowing organisms and large particle sizes (site 1), to values less than that of molecular diffusion in pure water (possibly the case at sites 4 and 5).

Care must be exercised in the use of reported molecular diffusion coefficients of substances within interstitial water, as the concentration of sorbed material which does not diffuse is often included with the material in solution (74). Concentration gradients based on the sum of sorbed and nonsorbed materials will lead to lower calculated diffusion coefficients than if only the material in solution were used to determine the gradients.

TIDAL MIXTURE

During August and September of 1970, a series of experiments were conducted at sites 1 and 4 in order to study the discharge and recharge process of tidal flat pore water during a tidal cycle (76).

During the first series of experiments at site 1, measurements of the hydraulic surface within the flats were obtained by means of pipes driven into the deposits. It was found, however, that the hydraulic response of the system was too slow. During later investigations, the hydraulic surface was measured through dug holes with the surface referenced to stakes of known elevation.

Changes of the hydraulic surface for three stations located at site 1 are shown in Fig. 31. The station elevations are shown on Fig. 32 and the free water surface elevations, which were measured during the sampling period shown on Fig. 33.

These results suggest that during the ebbing of the tide, pore water drains from those areas exposed by the tide. Drainage is along the beach, passing through the surface at the region above the free water surface. The slope of the hydraulic surface at approximately 2 hours after low tide is shown on Fig. 31. As seen in this diagram, the hydraulic surface meets the ground surface between stations C and D. Similar hydraulic surface profiles can be drawn for different times within the tidal cycle from the data given in Fig. 30. Thus, the data show that the flow of pore water during the ebbing tide and durin the low tide period results in a surface flow component at different elevations at different periods of the tidal cycle. The magnitude of this surface flow component depends on the permeabilities found at each location (see Table 15). During the tidal cycle, the hydraulic surface within the flats dropped by approximately 1.5 to 0.5 feet, the larger drops being measured at the higher elevations. Above the hydraulic surface, the water content was reduced to approximately 90 percent saturation. These percents, shown in Fig. 31, should only be considered as rough approximations due to the difficulty of obtaining undisturbed one-inch thick samples.

Using the mixing length description of the diffusion coefficient, the data presented above can be utilized to compute rough estimates of effective diffusion coefficients due to the tidal pore drainage described above. These effective diffusion coefficients are approximately 10 to 50 times greater than molecular diffusion coefficients (for oxygen) in water. In addition, oxygen may be introduced in large amounts to the unsaturated region.

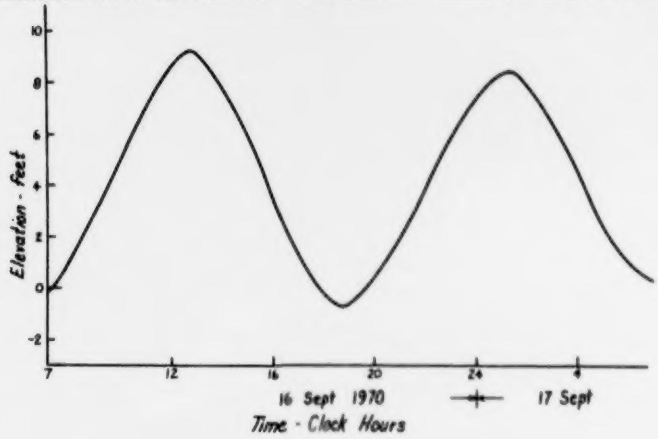


FIG. 31 - HYDRAULIC SURFACE DURING EXPERIMENTS AT SITE 1.

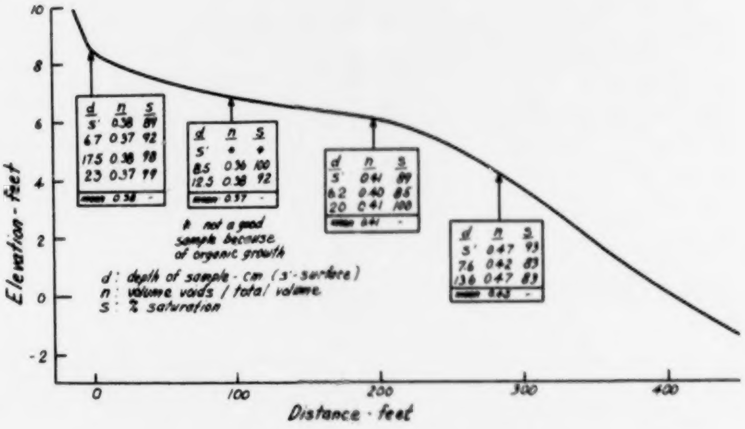


FIG. 32 - CONDITIONS AT SITE 1 DURING DRAINAGE EXPERIMENT.

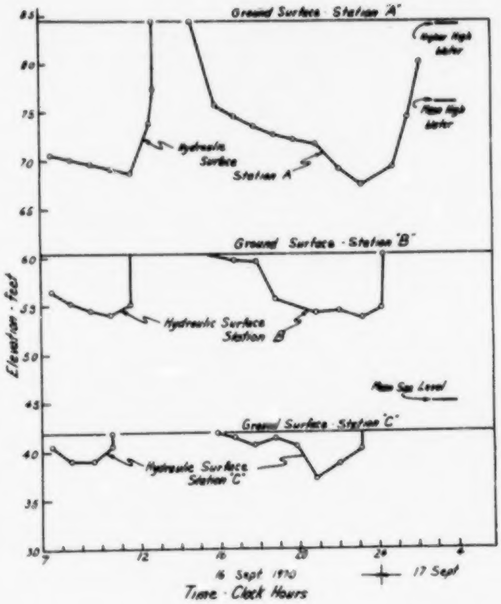


FIG. 33 - FREE WATER ELEVATIONS DURING EXPERIMENTS AT SITE 1.

TABLE 15. PERMEABILITY AND VOID RATIO AT SITE 1

Elevation (ft above MLLW)	Permeability (cm/min)	Vol. Voids/Total Vol.
8.3	0.04	0.38
6.8	0.0008[a]	--
6.0	--	0.36
6.0	--	0.38
3.8	--	0.44
1.7	--	0.44
-1.0	0.03	0.42

(a) Plant growth on surface

At site 4, no similar tidal drainage could be measured. Water would remain within pools (with some evaporation) until the flood tide covered flats. Vertical mixing was thus reduced to molecular diffusion and the turnover by organisms within the deposit. This later method did not appear to be substantial at site 4. Partial scour of the region was also noted, due to wave action as the tide rose and fell.

The characteristics of the deposits at sites 1 and 4 were quite different. The deposits at site 1 contained a reasonably uniform sand while large amounts of silts and clays were present at site 4. It appears that the difference in particle size was chiefly responsible for the differences in drainage characteristics and thus the differences in vertical mixing.

During the flood tide at site 1, the hydraulic surface began to rise slowly as the free surface approached a given elevation (see Fig. 31). This rise became abrupt at each location as the flooding waters covered that location. A more detailed description of this study has been presented (76).

PERIODIC SCOUR

Though time was not available to maintain a sufficient sampling program to define seasonal changes of conditions with the benthic systems of tidal flats the data available do suggest that periodic scour of the deposits, generally to a depth of 5-10 cm, is an important factor in determining these conditions. The scour due to wave action, high water velocities and extreme tides can result in a periodic oxidation of ferrous sulfide and a "recycling" of the iron. Such physical disruptions tend to prevent the depletion of available iron and the subsequent buildup and release of free sulfide. The influence of oxidizing conditions upon the concentrations of free sulfides is illustrated in Fig. 34 which is a composite of results from sites 1, 2, 4 and 5. The sulfates brought into the deposit as a result of a physical turnover may not provide for sufficient sulfate reduction to deplete the available iron. Depletion of available iron may thus require the additional diffusive transport of sulfate from the surface either through molecular diffusion or through partial (or limited) scour. Thus, the buildup of free sulfide is most likely within the top 5-10 cm. Periodic turnover of this region sufficiently to oxidize the ferrous sulfide, however, would prevent this buildup. The influence of such physical turnover is indicated by the progressive change in the total (acid solubl sulfides at site 4 as shown in Fig. 35 (free sulfide concentrations were below detectable levels). The change appears to be most significant above 10 cm. The decline of total sulfides as winter is approached reflects the declining

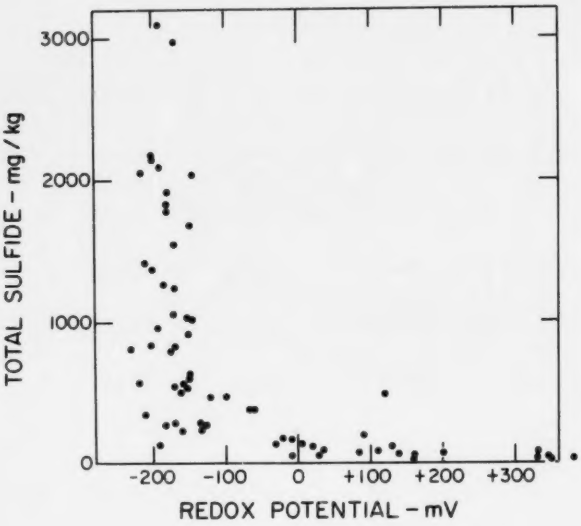


FIG. 34 - RELATIONSHIP BETWEEN TOTAL SULFIDES (ACID SOLUBLE) AND REDOX POTENTIAL WITHIN DEPOSITS AT SITES 1, 2, 4, and 5.

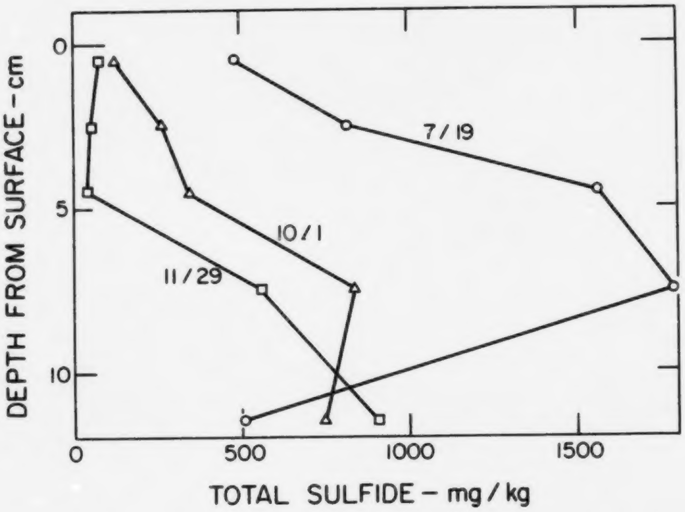


FIG. 35 - TEMPORAL CHANGE OF TOTAL SULFIDE (ACID SOLUBLE) PROFILES AT SITE 4.

salinity (and thus sulfates) during this period at this site. The trend may also reflect and increase wave action due to storms during this period.

A limited or partial scour or turnover of the upper layers of deposits may not be sufficient to result in any substantial oxidation of the ferrous sulfide. However, such limited scour can serve to transport sulfate into the deposit. A partial turnover which entrained overlying water into the sedimen would normally contain 4-10 mg/l of dissolved oxygen yet the sulfate concentration could be 2000 mg/l or greater. Thus limited turnover could contribut to a depletion of available iron and a buildup of free sulfide (generally wit the top 10 cm) if sufficient organics were available. Such limited scour in the absence of a more complete scour would be most likely to occur within protected areas (sloughs, diked areas, etc.) with relatively unconsolidated sediments of high organic content.

SECTION XIV

GENERAL BENTHIC DEPOSIT MODEL

GENERAL

As discussed in the introduction of this report, the basic approach employed in this study involved two distinctive features. These features were:

1. A complementary feedback occurred between the mathematical model studies and the experimental portions of the project.
2. The study was approached at several levels of resolution which complimented each other. That is sub-systems were viewed as integrated systems with component parts and these same sub-systems were also viewed as component parts of a higher level system.

The objective of this section of the report is to provide a benthic system model in the language of mathematics. The model will serve to integrate the principal processes shown in Fig. 2 and provide a framework for integrating the results previously discussed into the general benthic system. The specific mathematical description of each of these component processes will not, however, be given. Though the previous sections of this report do give insight into some of these component processes, particularly sulfate reduction, further definition must be based on continued feedback with experimental results.

The model will be developed by first stating the principal assumptions. Then, a description of the general distribution in space and time of soluble and insoluble materials within benthic systems will be provided. The major biochemical reactions which occur within benthic systems will then be presented in two slightly different models. The intent of presenting the second model, which is a simplified version of the first biochemical model, is to show how some simplifications can be made without necessarily sacrificing too much from the capabilities of the model. Finally, the distribution equations will be combined with the biochemical models to obtain two slightly different models which are relevant to environmental studies of benthic systems. The models are developed only for the benthic systems and do not here include the overlying air and water. The system described, however, is nearly applicable to the overlying water.

PRINCIPAL ASSUMPTIONS

Several principal assumptions and limitations of the model are listed below:

1. The model will be one-dimensional; considering only variations in the vertical direction.
2. The model will assume an equilibrium between sorbed and nonsorbed materials.
3. Compaction of deposits will not be included in the model.
4. It will be assumed that the biological reactions are not limited by the concentrations of the microorganisms.
5. Deposition and scour will not be explicitly described in the model. However, the model description is such that numerical simulations based on the model will be able to accommodate a wide variety of deposition and scour patterns.
6. As in all models, many different substances will be grouped into large categories. As an example, degradable organics will be grouped into two categories (insoluble and soluble). If necessary, these groupings may be broken down further.

GENERAL DESCRIPTION OF SOLUBLE MATERIALS

Consider a vertical section of deposit of cross-sectional area A with a fixed reference ($z=0$) at some depth below the surface of the deposit. Positive depth, z, is measured from this reference toward the surface. A positive interstitial water velocity is in the upward direction and a positive concentration gradient indicates an increasing concentration from the reference to the surface. Taking a mass balance on a slice of depth dz within the deposit leads to

$$\frac{\partial(AndzS')}{\partial t} = F_i - F_o + nAdz\Sigma G + Adz\Sigma H \qquad (29)$$

in which n is the fraction of the deposit filled with water, S' is the concentration of a soluble material, within the interstitial water, F_i is the total flux of this substance into the slice, F_o is the flux of the substance out of the slice, ΣG is the sum of the sources and sinks of the soluble material from within the interstitial water and ΣH is the sum of the sources and sinks of the soluble substance from insoluble states. Hereafter the prefix, G, for biochemical reactions will denote a rate of mass change or transfer per unit volume of interstitial water. The prefix, H, will denote a rate of mass change or transfer per unit volume of wet sediment.

The flux of S' due to advection and diffusion is taken as

$$F = -D_{s'}Am\frac{\partial S'}{\partial z} + UAmS' \qquad (30)$$

in which $D_{s'}$ is the vertical diffusion coefficient for S', U is the vertical velocity (positive upward) and m is the fraction of A open to diffusion and advection. Let

$$F_o = F_i + \frac{\partial F}{\partial z}dz \qquad (31)$$

Substituting equations (30) and (31) into equation (29) leads to

$$\frac{\partial(AnS')}{\partial t} = \frac{\partial(D_{s'}Am\partial S'/\partial z)}{\partial z} - \frac{\partial(UAmS')}{\partial z} + nA\Sigma G + A\Sigma H \qquad (32)$$

Assuming A to be constant with distance and time and n to be constant with time reduces equation (32) to

$$\frac{\partial S'}{\partial t} = \frac{1}{n}\,\frac{\partial(D_{s'}m(\partial S'/\partial z))}{\partial z} - \frac{1}{n}\,\frac{\partial(UmS')}{\partial z} + \Sigma G + \frac{\Sigma H}{n} \qquad (33)$$

If $D_{s'}$, U, n, and m are further considered as constant with depth and if n is set equal to m, equation (33) reduces to

$$\frac{\partial S'}{\partial t} = D_{s'}\,\frac{\partial^2 S'}{\partial z^2} - U\frac{\partial S'}{\partial z} + \Sigma G + \frac{\Sigma H}{n} \qquad (34)$$

For simplicity, equation (34) will be expanded to include the biochemical reactions rather than the more general equation (33). The biochemical reactions presented herein can be easily be accommodated into equation (33) if desired.

GENERAL EQUATION OF INSOLUBLE MATERIALS

Following a similar mass balance as above, one obtains the general equation for insoluble materials shown below

$$\frac{\partial I'}{\partial t} = \Sigma H + n\Sigma G \qquad (35)$$

in which I' is the concentration (mass per unit volume of wet sediment) of the insoluble materials.

BIOCHEMICAL MODEL I

The primary biochemical reactions occurring within the estuarine benthic systems (see Fig. 2 and Section IV) are shown in the simplified mass transfer diagram of Fig. 36. Definition of terms is given in Table 16.

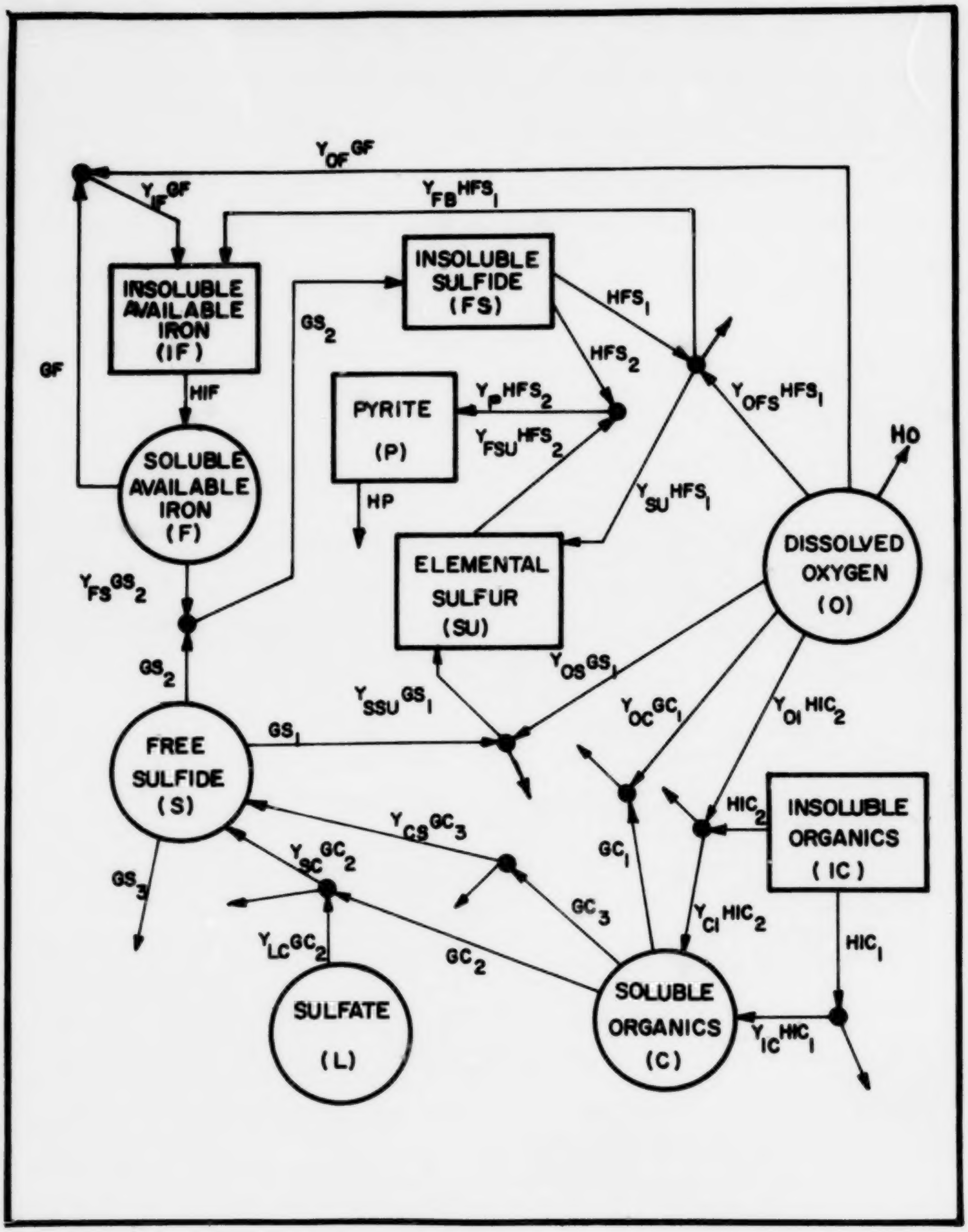

$Y_{OF}GF$
$Y_{IF}GF$
$Y_{FB}HFS_1$
INSOLUBLE AVAILABLE IRON (IF)
INSOLUBLE SULFIDE (FS)
GS_2
GF
HIF
HFS_1
HFS_2
PYRITE (P)
$Y_P HFS_2$
$Y_{FSU}HFS_2$
$Y_{OFS}HFS_1$
HO
SOLUBLE AVAILABLE IRON (F)
HP
$Y_{SU}HFS_1$
ELEMENTAL SULFUR (SU)
DISSOLVED OXYGEN (O)
$Y_{FS}GS_2$
GS_2
$Y_{OS}GS_1$
$Y_{SSU}GS_1$
$Y_{OC}GC_1$
$Y_{OI}HIC_2$
FREE SULFIDE (S)
GS_1
HIC_2
INSOLUBLE ORGANICS (IC)
$Y_{CS}GC_3$
$Y_{SC}GC_2$
GC_1
GS_3
GC_3
$Y_{CI}HIC_2$
HIC_1
$Y_{LC}GC_2$
GC_2
SULFATE (L)
SOLUBLE ORGANICS (C)
$Y_{IC}HIC_1$

FIG. 36 - BIOCHEMICAL MODEL I FOR ESTUARINE BENTHIC SYSTEM. (Available Iron also includes other metals which form insoluble sulfides; Zn, Sn, Cd, Hg and Cu.)

TABLE 16. DEFINITION OF TERMS FOR BIOCHEMICAL MODEL I OF ESTUARINE BENTHIC SYSTEM

GC_1 = the aerobic biochemical degradation of soluble organics,

GC_2 = the degradation of soluble organics by sulfate reduction,

GC_3 = the non sulfate reduction anaerobic biochemical degradation of soluble organics,

GF = the oxidation of soluble available iron to insoluble available iron,

GS_1 = the oxidation of free sulfides (primarily, chemical reaction with dissolved oxygen but also due to aerobic autotrophic bacteria),

GS_2 = the reaction of free sulfides with soluble available iron (and other materials which form insoluble sulfides),

GS_3 = the loss of free sulfide through photosynthetic anaerobic sulfur bacteria,

HFS_1 = the oxidation of insoluble sulfides (primarily ferrous sulfide) with dissolved oxygen,

HFS_2 = the oxidation of insoluble ferrous sulfides with elemental sulfur,

HIC_1 = the solubilization of organics under anaerobic conditions,

HIC_2 = the solubilization of organics under aerobic conditions,

HIF = the solubilization of available iron,

HO = the dissolved oxygen demand due to other causes (e.g., oxidation of ammonia, benthic plant respiration),

HP = the oxidation of pyrite under aerobic conditions,

Y_{CI} = mass of soluble organic carbon per mass of insoluble organic carbon solubilized under aerobic conditions,

Y_{CS} = mass of sulfide produced per mass of organic carbon utilized in non-sulfate reduction anaerobic decomposition,

Y_{FB} = mass of insoluble available iron per mass of insoluble sulfide oxidized,

Y_{FS} = mass of available iron per mass of free sulfide reacted to form insoluble sulfides

Y_{FSU} = mass of elemental sulfur used per mass of insoluble sulfide transformed to pyrite,

Y_{IC} = mass of soluble organic carbon per mass of insoluble organic carbon solubilized under anaerobic conditions,

Y_{LC} = mass of sulfate per mass of soluble organic carbon utilized in sulfate reduction,

Y_{OC} = mass of oxygen per mass of soluble organic carbon oxidized,

TABLE 16. Cont.

Y_{OF} = mass of oxygen per mass of soluble iron oxidized,

Y_{OFS} = mass of oxygen per mass of insoluble sulfide oxidized,

Y_{OI} = mass of oxygen utilized per mass of insoluble organic carbon solubilized,

Y_{OS} = mass of oxygen per mass of free sulfide oxidized,

Y_{P} = mass of pyrite formed per mass of insoluble sulfide reacted with elemental sulfur,

Y_{SC} = mass of sulfate produced per mass of soluble organic carbon utilized in sulfate reduction,

Y_{SU} = mass of elemental sulfur per mass of insoluble sulfided aerobically oxidized,

Y_{SSU} = mass of elemental sulfur per mass of free sulfide oxidized.

Insoluble materials are shown in the rectangles while soluble materials are shown in the circles of Fig. 36. Symbols used to designate concentrations of materials are given in Fig. 36. Concentrations of soluble materials are given in mass per unit volume of interstitial water while concentrations of insoluble materials are given in mass per unit volume of wet sediment. A principal assumption which led from Fig. 2 to Fig. 36 is that the biochemical reactions are not limited by the concentrations of micro-organisms.

The relative significance of the different reactions shown in Fig. 36 and Table 16 will depend on the conditions within the benthic system (See Chapter IV). Three benthic conditions and the relative importance of the reactions within these conditions are given in Table 17. The aerobic regions, (portions of the benthic system containing dissolved oxygen) are generally located within the top few millimeters of the deposit. Such regions also frequently line burrows within deposits. Aerobic conditions are also found for short periods of time after the deposit has been physically overturned. If organic material is sufficient, an anaerobic region within which sulfate reduction takes place is normally located below the aerobic region. If organics are high, sulfate may become limiting within several centimeters of the surface.

Microbial decomposition may occur below the depth of the sulfate limitation. Free sulfides may diffuse from above and react with available iron in this region. In addition, organics and iron may be solubilized in this region and diffuse upward into the region of sulfate reduction. Methane fermentation within this deep region may result in a physical disruption of the deposit above.

The biochemical reactions shown in Fig. 36 and Table 16 may be combined with equations (34) and (35) to provide the following mathematical description of the benthic system.

TABLE 17. DEPENDENCE OF REACTIONS OF BIOCHEMICAL MODEL I ON INTERNAL BENTHIC CONDITIONS

Reaction	Aerobic Region(a)	Anaerobic-Sulfate Reduction Region (b)	Anaerobic, No Sulfate Reduction Region (c)
HIC_1	none	significant	significant (d)
HIC_2	significant	none	none
GC_1	significant	none	none
GC_2	none	significant	none
GC_3	none	slight (e)	significant (d) (f)
HO	significant	none	none
GS_1	significant (g)	none	none
GS_2	very slight	significant	conditional (h)
GS_3	none	slight (i)	unlikely (i)
GF	significant	none	none
HIF	slight	significant	significant
HFS_1	significant (g) (k)	none	none
HFS_2	none	significant (d) (j)	normally slight (d) (j)
HP	slight (j) (1)	none	none

(a) DO $>$ 0.1 mg/1; upper region of sediment

(b) DO $<$ 0.1 mg/1; $SO_4 >$ 10-50 mg/1; below aerobic region

(c) DO $<$ 0.1 mg/1; $SO_4 <$ 10-50 mg/1; below sulfate reduction region

(d) likely decreasing with depth

(e) normally $Y_{SC}GC_2 > Y_{CS}GC_3$

(f) if conditions favorable (e.g., available degradable organics, no loxic levels of free sulfides)

(g) normally small suflate source in comparison to diffusive transport and exhange due to disturbance of bottom

(h) largely dependent upon diffusion of free sulfides from sulfate reduction region

(i) light needed

(j) long term significance; time scale of weeks to years

(k) likely to occur after sediment overturned or flushed with oxygenated water

(1) not included as oxygen loss due to relative slowness or reaction

Insoluble carbon:

$$\frac{\partial IC}{\partial t} = - HIC_1 - HIC_2 \tag{36}$$

Soluble carbon:

$$\frac{\partial C}{\partial t} = D_C \frac{\partial^2 C}{\partial z^2} - U \frac{\partial C}{\partial z} + \frac{1}{n} (Y_{IC} HIC_1 + Y_{CI} HIC_2)$$

$$- GC_1 - GC_2 - GC_3 \tag{37}$$

Dissolved oxygen:

$$\frac{\partial O}{\partial t} = D_O \frac{\partial^2 O}{\partial z^2} - U \frac{\partial O}{\partial z} - Y_{OC} GC_1 - Y_{OS} GS_1 - Y_{OF} GF$$

$$- \frac{1}{n} (Y_{OI} HIC_2 + Y_{OFS} HFS_1 - HO) \tag{38}$$

Free sulfide:

$$\frac{\partial S}{\partial t} = D_S \frac{\partial^2 S}{\partial z^2} - U \frac{\partial S}{\partial z} + Y_{SC} GC_2 + Y_{CS} GC_3 - GS_1 - GS_2 - GS_3 \tag{39}$$

Sulfate:

$$\frac{\partial L}{\partial t} = D_L \frac{\partial^2 L}{\partial z^2} - U \frac{\partial L}{\partial z} - Y_{LC} GC_2 \tag{40}$$

Insoluble iron (and other material which form insoluble sulfides):

$$\frac{\partial IF}{\partial t} = Y_{FS}HFS_1 - HIF + nY_{IF}GF \tag{41}$$

Insoluble sulfides:

$$\frac{\partial FS}{\partial t} = nGS_2 - HFS_1 - HFS_2 \tag{42}$$

Soluble iron (and other material which forms insoluble sulfides):

$$\frac{\partial F}{\partial t} = D_F \frac{\partial^2 F}{\partial z^2} - U\frac{\partial F}{dz} + \frac{HIF}{n} - Y_{FS}GS_2 - GF \tag{43}$$

Elemental sulfur:

$$\frac{\partial SU}{\partial t} = Y_{SU}HFS_1 - Y_{FSU}HFS_2 + nY_{SSU}GS_1 \tag{44}$$

Pyrite:

$$\frac{\partial P}{\partial t} = Y_p HFS_2 - HP \tag{45}$$

For simplicity, a number of the normally less significant material transfers have been omitted from the model. As an example, the additions of sulfate from reactions GS_2 and HFS_1 have been omitted because these additions will normally be significantly smaller than the diffusive transport and the exchange due to the disruption of the sediment.

BIOCHEMICAL MODEL II

The biochemical model shown in Fig. 37 and Table 18 is similar to that shown above. Organics and available iron, however, are included in a single component which is considered insoluble and pyrite is not included (pyrite

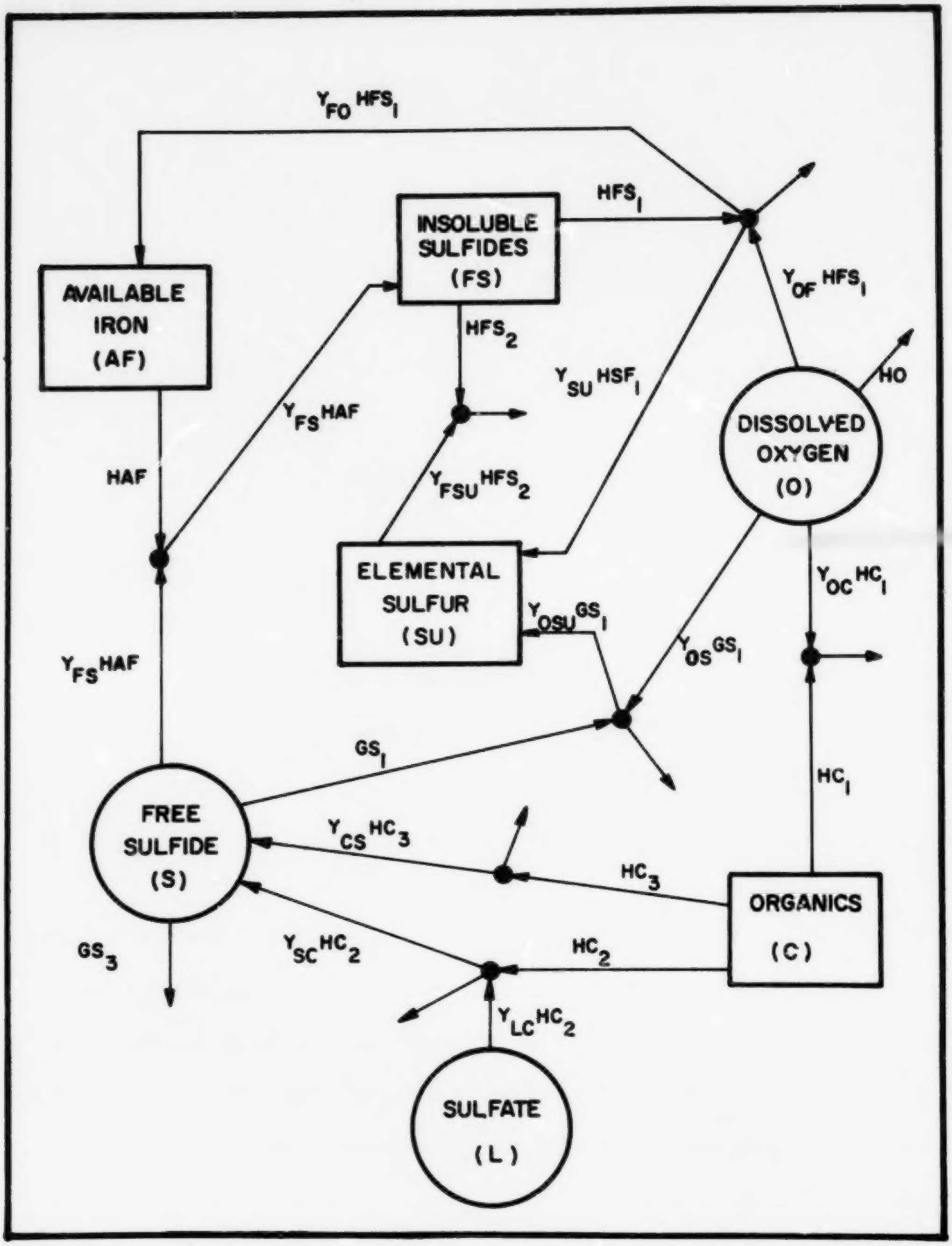

Y_FO HFS_1
INSOLUBLE SULFIDES (FS)
HFS_1
AVAILABLE IRON (AF)
Y_OF HFS_1
HFS_2
Y_SU HSF_1
HO
Y_FS HAF
DISSOLVED OXYGEN (O)
HAF
Y_FSU HFS_2
ELEMENTAL SULFUR (SU)
Y_OC HC_1
Y_OSU GS_1
Y_OS GS_1
Y_FS HAF
GS_1
HC_1
FREE SULFIDE (S)
Y_CS HC_3
HC_3
ORGANICS (C)
GS_3
Y_SC HC_2
HC_2
Y_LC HC_2
SULFATE (L)

FIG. 37 - BIOCHEMICAL MODEL II FOR ESTUARINE BENTHIC SYSTEM. (Available Iron also includes other metals which form insoluble sulfides; Zn, Sn, Cd, Hg and Cu.)

TABLE 18. DEFINITION OF TERMS FOR BIOCHEMICAL MODEL II OF ESTUARINE BENTHIC SYSTEM

GS_1 = the oxidation of free sulfides

GS_3 = the loss of free sulfides through photosynthetic anaerobic sulfur bacteria,

HAF = the reaction of available iron with free sulfides,

HC_1 = the aerobic biochemical degradation of organics,

HC_2 = the degradation of organics by sulfate reduction,

HC_3 = the non sulfate reduction anaerobic biochemical degradation of organics,

HO = the dissolved oxygen demand due to other causes (e.g., oxidation of ammonia, benthic plant respiration),

HFS_1 = the oxidation of insoluble sulfides with dissolved oxygen,

HFS_2 = the reaction of insoluble sulfides with elemental sulfur to form pyrite,

Y_{CS} = mass of sulfide produced per mass of organic carbon utilized in non-sulfate reduction anaerobic decomposition,

Y_{FB} = mass of available iron per mass of insoluble sulfide (primarily ferrous sulfide) oxidized,

Y_{FS} = mass of sulfide per mass of available iron reacted to form insoluble sulfides,

Y_{FSU} = mass of elemental sulfur used per mass of insoluble sulfide transformed to pyrite,

Y_{LC} = mass of sulfate per mass of organic carbon utilized in sulfate reduction,

Y_{OC} = mass of oxygen used per mass of organic carbon oxidized,

Y_{OF} = mass of oxygen used per mass of insoluble sulfide oxidized,

Y_{OS} = mass of oxygen used per mass of free sulfide oxidized,

Y_{SC} = mass of sulfide produced per mass of organic carbon utilized in sulfate reduction,

Y_{SU} = mass of elemental sulfur per mass of insoluble sulfides aerobically oxidized,

Y_{SSU} = mass of elemental sulfur per mass of free sulfide oxidized, and

TABLE 19. DEPENDENCE OF REACTIONS OF LOWER RESOLUTION MODEL (MODEL II) ON BENTHIC CONDITIONS

Reaction	Aerobic Region(a)	Anaerobic-Sulfate Reduction Region(b)	Anaerobic, No Sulfate Reduction Region (c)
HC_1	significant	none	none
HC_2	none	significant	none
HC_3	none	slight (d)	significant (e) (f)
HO	significant	none	none
GS_1	significant (g)	none	none
GS_3	none	slight (h)	unlikely (h)
HAF	very slight	significant	conditional (i)
HFS_1	significant (g) (k)	none	none
HFS_2	none	significant (e) (j)	normally slight (e) (j)

(a) $DO > 0.1$ mg/l; upper region of sediment

(b) $DO < 0.1$ mg/l; $SO_4 > 10\text{-}50$ mg/l; below aerobic region

(c) $DO < 0.1$ mg/l; $SO_4 < 10\text{-}50$ mg/l; below sulfate reduction region

(d) usually $Y_{SO}HC_2 > Y_{CS}HC_3$

(e) likely decreasing with depth

(f) if conditions favorable (e.g., available degradable organics, no toxic levels fo free sulfides)

(g) normally small sulfate source in comparison to diffusive transport and exchange due to distrubance of bottom

(h) light needed

(i) largely dependent upon diffusion of free sulfides from sulfate reduction region

(j) long term significance; time scale of weeks to years

(k) likely to occur after sediment overturned or flushed with oxydenated water

(l) small fraction of oxygen demand, primarily biological can be simply added). The increased simplicity of model 2, however, is purchased by a loss of "reality" in the model. Nevertheless, model 2 may be sufficient for most investigations and the greater simplicity may be advantageous. The relative significance of the reactions of model 2 to benthic conditions is given in Table 19. The biochemical reactions shown in Fig. 37 and Table 18 are combined with equations (34) and (35) to provide the following mathematical description of the benthic system.

Organic carbon:

$$\frac{\partial C}{\partial t} = -HC_1 - HC_2 - HC_3 \tag{46}$$

Dissolved oxygen:

$$\frac{\partial O}{\partial t} = D_O \frac{\partial^2 O}{\partial z^2} - U\frac{\partial O}{\partial z} - Y_{OS}GS_1 - \frac{1}{n}\left(Y_{OC}HC_1 - Y_{OF}HFS_1 - HO\right) \tag{47}$$

Free sulfide:

$$\frac{\partial S}{\partial t} = D_s \frac{\partial S^2}{\partial z^2} - U\frac{\partial S}{\partial z} + \frac{1}{n}\left(Y_{CS}HC_3 + Y_{SC}HC_2 - Y_{FS}HAF\right) - GS_1 - GS_3 \tag{48}$$

Sulfate:

$$\frac{\partial L}{\partial t} = D_L \frac{\partial L^2}{\partial z^2} - U\frac{\partial L}{\partial z} - \frac{Y_{LC}HC_2}{n} \tag{49}$$

Available Iron (and other materials which form insoluble sulfides):

$$\frac{\partial AF}{\partial t} = Y_{FO}HFS_1 - HAF \qquad (50)$$

Insoluble sulfides:

$$\frac{\partial FS}{\partial t} = Y_{FS}HAF - HFS_1 - HFS_2 \qquad (51)$$

Elemental sulfur:

$$\frac{\partial SU}{\partial t} = Y_{SU}HFS_1 - Y_{FSU}HFS_2 + n\, Y_{OSU}\, GS_1 \qquad (52)$$

SECTION XV

ENVIRONMENTAL IMPLICATIONS FOR ESTUARINE BENTHIC SYSTEMS

GENERAL IMPLICATIONS

The conditions within estaurine benthic systems have important influences on the functioning of estaurine systems. The interfacial and benthic regions are themselves significant regions of estuarine systems. Moreover, the overlying water quality can be strongly influenced by the conditions within the benthic system. Depletion of dissolved oxygen and toxic concentrations of free sulfide may result.

Benthic conditions, particularly within tidal flat areas, may have significant influences on air quality. The release of sulfur to the atmosphere as a result of sulfate reduction within coastal regions may be of the same order of magnitude as the buring of fossil fuels (25)(26)(27). If one assumes that the total area of estuaries is 1,222,000, km^2 (77) then an average estuarine benthic atmosphere sulfur release of 0.1 gm/m^2-day would be sufficient to be approximately equal to the annual world sulfur release from the burning of fossil fuels, 50 X 10^6 tons/yr. This figure does not include the influence of bays, seas, deltas,shoreline areas, saline lakes, etc.

The total magnitude of benthic sulfide release to the atmosphere and the nature and extent of man's activities which would contribute toward an increased sulfur release are subjects of major concern. The quantitative evaluation of these subjects is beyond the scope of this report. It is possible however to describe a variety of activities which can result in a variety of changes within the benthic systems of environmental concern. To facilitate the following discussion, reference will be made to the classification system described in Chapter VI and specifically to Table 6 and Fig. 12. The possible influences of man's activities on estuarine benthic systems are briefly discussed. Reference to Fig. 2 will help to clarify these discussions.

CHANGES IN ORGANIC DEPOSITION

A general increase of organic deposition to benthic systems can result from the input to the estuary of additional organics (such as from waste outfalls), from the input of inorganic nutrients which lead to an increase of primary production within the estuary, or to the deposition of organics re-suspended at some other location. Such increases result in a shift of benthic states toward region 5 (see Fig. 12). Dredging operations can, however, remove organics from previously degraded systems and thus assist in their recovery.

CHANGES IN INORGANIC DEPOSITION

Increased deposition of inorganic material can result in suffocating benthic plants and animals. Toxic materials in these deposits can also harm these communities. Again, controlled removal of toxic materials by dredging may assist degraded systems to recover.

Potential problems can also occur from reduced sediment transport to estuaries due to upstream dams, jetties, channelization, and reduction of seasonal sediment scouring. Such reduction may lead to a lowered input of available iron to the systems and thus result in a shift toward regions 4 and 5 of Fig. 12. This shift would be most pronounced if a general increase in organic deposition also occurred.

CONSTRUCTION OF DIKES, JETTIES, WHARVES, ETC.

Dikes, jetties, wharves, etc. can alter estuarine ecosystems in several ways. These structures may provide a solid substream on which a highly diverse population of attached plants and animals may develop. However, they can isolate regions from the estuarine system, thus drastically altering their nature and function. Partial diking of a tidal flat region can lead to an increased trapping of organics and fine particles. In addition, such dikes can reduce the more significant periodic scour and thus reduce the "recycling" of iron. Benthic systems within such regions may shift to a type 5 system, as appears to be the case at site 5 investigated in this report.

HYDRODYNAMIC CHANGES

Deepening of channels, filling of tidelands, construction of dikes and jetties, stabilization of banks and other such activities all serve to change the hydrodynamic regime of estuaries. Changes in advective and diffusive transport and scour can result in significant changes in organic deposition, inorganic deposition, salinity distributions, temperature distribution, distribution of pelagic life stages, inorganic nutrient distribution, dissolved oxygen distribution and other environmental factors which influence the estuarine ecosystem in complex (and often unknown) ways; often these changes show themselves most graphically in altered plant and animal distributions. Changes which tend to reduce scour may lead to a shift to type 5 systems. Extremely unstable bottoms may prevent the establishment of stable benthic communities. Reduction of seasonal salinity variations can disrupt biological cycles, lead to an increased development of resident populations at the expense of migrating populations and can contribute to a benthic system shift toward type 5 by reducing the seasonaly variation in sulfate supply to benthic systems.

TIDELAND FILLING

Filling tideland with dredging spoils or other materials can have widespread adverse effects in an estuary. In general, tidal flats are highly productive areas contributing a major portion of the food to an estuary. Covering of this valuable tideland can be critical, not only because food sources are removed but because the total high tide volume of the estuary is reduced. Many estuarine fishes live in the channels at low tide and move over the tidal flats as the tide rises to feed (a habit of fishes which may account for better fishing on an incoming tide). Likewise, shore birds and a few mammals move into the exposed areas at low tide to feed. The variety of species which function at some stage of their life cycle in the tidelands is great. When tidelands become covered, diversity is thus likely reduced.

Within a given estuary a wide range of localized inorganic and organic benthic depostion rates, DO concentrations, sulfate concentrations, scour velocities, and other factors determine estuarine benthic types that can be expected. These conditions, moveover, will change with time. Thus, differences can be expected over temporal and spacial dimensions of any estuary. Within unpolluted regions of estuaries, benthic types 1, 2 and 3 will likely predominate. The wide variety of benthic systems normally found in tidal estuaries makes possible a larger biological diversity which, in turn, likely contributes to the functioning of the entire estuarine system.

A wide range of man's activities can produce significant changes in temporal and spacial distribution of benthic types. Such changes can result in a decrease in the variety of benthic systems within space and time. Such a reduction of system diversity, if extensive, would likely reduce biological diversity. Man's activities might also result in a general shift, likely toward benthic type 5 (region 5 of Fig.12) which would be considered undesirabl because of lower DO concentrations and higher free sulfide concentrations.

Environmental changes often cannot be explained by a simple casual relationship to a single activity. Thus, the environmental impact of any particular activity, must be considered along with a host of other activities (both man-made and natural).

TRANSIENT CONDITIONS DUE TO DREDGING

Dredging of type 4 and 5 benthic systems would likely have a greater immediate impact on water quality than would the dredging of types 1, 2 and 3. The release of free sulfide would be most objectionable because of its oxygen demand and its toxicity. However, because of the rapid reaction rate of free sulfides and oxygen in estuarine waters, the short term release of free sulfide during dredging of sludge deposits might be preferable to the long term release by undisturbed deposits. Thus, in some cases, dredging operations could be used to assist the recovery of a system which had been degraded to a type 5 system. Such dredging, however, could release heavy metals which had been held in the deposits as insoluble sulfides. Heavy metals such as mercury and cadmium could have both short term and long term toxic effects.

Increased turbidity due to dredging operations can decrease light penetrations, and thereby reduce photosynthesis. It can cause mechanical blockage of gills and ultimate suffocation of many species, simply because the gills cannot absorb enough oxygen from the water. Likewise, food filtering mechanisms, which are often associated with respiratory organs, may also become blocked by too many particles in the water.

The settling of fine sediment from turbid waters over benthic species may have catastrophic effects on life cycles if pelagic larva or eggs cannot leave the sediments or if pelagic larvae are prevented from settling in a satisfactory environment. For example, oyster spat cannot attach to the necessary shell substratum if this shell is covered with a layer of fine sediment.

The type of benthic system that develops at a given location can be dependent on the biological turnover previously discussed. A transient environmental condition, such as a temporary depletion of dissolved oxygen, could eliminate a community which is contributing to this turnover. A new benthic type might then develop. The re-establishment of the previous community might not be immediately possible due to this change in type even though the unfavorable environmental condition which caused this change had passed. Thus, periodic unfavorable conditions could have a continuous influence on benthic systems.

LONG TERM PARTICLE SIZE CHANGE

Significant long-term decreases in sediment particle sizes within developed estuaries can occur (78) . Adequate data to demonstrate such long-term decreases, however, are not available for most tidal estuaries. Decreases in particle size may occur as a result of upstream dams, continued dredging, construction of jetties, and other similar activities. Particle size reduction could significantly decrease the permeability of deposits and thus contribute toward reduced transport of exogenous hydrogen acceptors This would in turn lead to a reduction, to the left, of regions 1 and 2 of Fig. 12. A reduction of particle size may also impair the movement of certain benthic animals within deposits.

SPOIL DISPOSAL

Sediment removal and spoil disposal can result in a shift in benthic types at both the sites of sediment removal and disposal. As an example, the oxidation of sulfides and organics during the removal and disposal operations might result in a shift from an original type 5 system at the removal site to a type 2 or 3 system at both sites. The reverse may occur, however, if during disposal, differential settlings of organics and inorganics occurred. After settling, the spoil deposits may shift toward type 5 due to the higher organics within the upper regions of the deposits.

SECTION XVI

LOWER LEVEL RESOLUTION STUDIES

GENERAL

In the earlier phases of this study, a conventional viewpoint of estuarine systems was employed which dealt with the estuary as an elongated water body subject to tidal influences. A mathematical model was developed which, though having a number of unique features, reflected the same estuarine systems view as the common one and two dimensional estuarine models. Field studies of tidal hydrodynamics and mixing processes were conducted to compliment the mathematical model studies. As previously discussed, the study shifted emphasis to a finer level of resolution in which estuarine benthic systems were examined.

The latter stages of the study were dominated by this finer level of resolution view which has been described in the previous chapters. During the course of this study, a number of subjects principally related to the lower level resolution view were examined. The principal results of these examinations are briefly discussed in the following subsections. Reference is made to the publications which provide specific details and a description of the general estuarine model employed is given in the appendix.

ADVECTION ERRORS

A basic component of most water quality models involves the advection o movement of materials by flowing waters. The errors associated with several finite difference models of advection were examined. These errors were found to distort model results and these errors were most apparent when the advection of slug loads was simulated. The tendency to numerically spread materials was found to be a common error, along with the production of oscillations and a tendency to skew distributions. A method of estimating and controlling these errors was developed and examined. Details of this phase of the study are found in the following reference.

REFERENCE: Bella, David A., and Grenney, William J., "Finite-Difference Convection Errors," Journal of the Sanitary Engineering Division, ASCE, Vol. 96, No. SA6, Proc. Paper 7744, December, 1970, pp. 1361-1375.

ESTIMATING DISPERSION COEFFICIENTS IN ESTUARIES

Two general methods of determining longitudinal dispersion coefficients from estuarine salinity profiles (79)(80)(81) were examined. In addition a third method was developed. The adequacy of these three methods was examined through the use of the finite difference estuarine model. Methods which employed the assumption of a steady state were found to be seriously deficient when river flows varied. This general conclusion was in agreement with the work of Ward and Fisher (82). The method developed in this study was found to be the most accurate of the three tested. Details are provided in the following reference.

REFERENCE: Bella, D.A., and Grenney, W.J., "Estimating Dispersion Coefficients in Estuaries," (technical note), Journal of the Hydraulics Division, ASCE, Vol. 98, No. HY3, March 1972.

SLACK WATER BUILD-UP IN ESTUARIES

A series of model runs were conducted in which tidal variations were included. The Yaquina estuary served as the prototype, although a great deal of the effort was not spent to model the Yaquina in detail. The results indicated that pollutant profiles within estuaries were generally far more sensitive to variations in the biochemical reactions than to the dispersion coefficients or tidal variations. This result had a major influence in directing the study toward the biochemical reactions.

These studies did demonstrate, however, the high pollutant concentration could develop in the vicinity of an outfall during the slack water period. This pollutant accumulation was studied through the mathematical model and a field study.

A diffuser was installed across the main channel of the Yaquina River about 35 Km from the mouth, at Newport, Oregon. Rhodamine-B was injected at a constant rate for a ten hour period and more than 400 samples were collected. The data indicate a significant build-up during periods of slack water. The model results simulated average observed trends reasonably well, however, calculated peaks were lower than the field observations. Details are provided in the following reference.

REFERENCE: Grenney, W. J. and Bella, D. A., "Field Study and Mathematic Model of the Slack Water Build-up of a Pollutant in a Tidal River," Limnology and Oceanography, Vol. 17, No. 2, March 1972.

TIDAL MEASUREMENTS

During the initial phases of this study, partial support was given to field studies of tidal elevations and tidal currents in the Yaquina, Alsea, and Siletz estuaries. Because of the changing emphasis of the study reporte herein, continued support for tidal measurement was later provided through the Sea Grant Program (NSF), Ocean Engineering, Oregon State University. Results of the supported studies are provided in the following reference.

REFERENCE: Goodwin, C.R., Emmet, E. W., and Glenne, B., "Tidal Study o Three Oregon Estuaries," Bulletin No. 45, Engineering Experiment Statio Oregon State University, Corvallis, Oregon, May 1970.

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SECTION XIX

FINITE DIFFERENCE MODEL

INTRODUCTION

The purpose of this appendix is to provide a description of the finite difference estuarine model which was used in the early phases of this research project. The model was developed for the research project and the following three basic criteria were used in its selection:

(1) The model should be accurate.

(2) The model should be simple and flexible so that many revisions could be made.

(3) The model should be reasonably efficient with respect to computer time.

It was not the intent of the investigators to develop a standard computer program for general use. We have found, however, that the finite difference methods selected and described herein are relatively simple (particularly the water quality model) and thus they should be of general use. Only a first order biochemical reaction will be presented below, however, the methods presented can be simply adapted to a wide variety of biochemical reactions and processes.

This appendix is based principally upon two references (Grenney, 1970 and Bella, 1972) and referral to them should be made for additional informatio

GENERAL STRUCTURE

The main computer program is based on the finite-difference method developed by Bella and Dobbins (46). The stream channel is divided into equal length segments (ΔX) and the mass within each segment is computed for finite time increments (ΔT). In this model, ΔT is less than a tidal cycle. Segments are labeled beginning with segment one at the fresh water end of the channel as shown in Figure A1, where N = segment number on the main channel and n = interface number. The program is versatile in that irregular estuary configurations can be simulated by appropriate arrangement of the segments. Tributaries can be attached to the main channel as shown in Figure A1 where K_n are segment numbers of the tributary intersecting the main channel at segment N. Mud flats can be simulated by a series of adjacent short tributaries where material is transferred across all four interfaces of each interior segment. A two-dimensional effect can be achieved by superimposing two or more channels.

The program was written in Fortran IV for use on the CDC 3300 computer at Oregon State University. Figure A2 is a flow diagram of the main program. Four types of input data are required:

1. Finite-difference grid parameters ΔX and ΔT. The amount of numerical error introduced by the finite-difference scheme was found to be very sensitive to these parameters (See Bella and Grenney, 1970).
2. Estuary configuration consisting of the cross section area, channel side slopes, and mean water depth at each segment and the location and configuration of each tributary.
3. Hydraulic characteristics of the main channel and each tributary. These data include magnitude of tidal wave at the mouth, speed of tidal wave propagation, channel friction, and fresh water inflow rates.
4. Mass transfer parameters and initial conditions. Those data include the dispersion and decay coefficients and the initial pollution concentration in each segment. Also included is the location of pollution sources and the rate of pollution injection at each source.

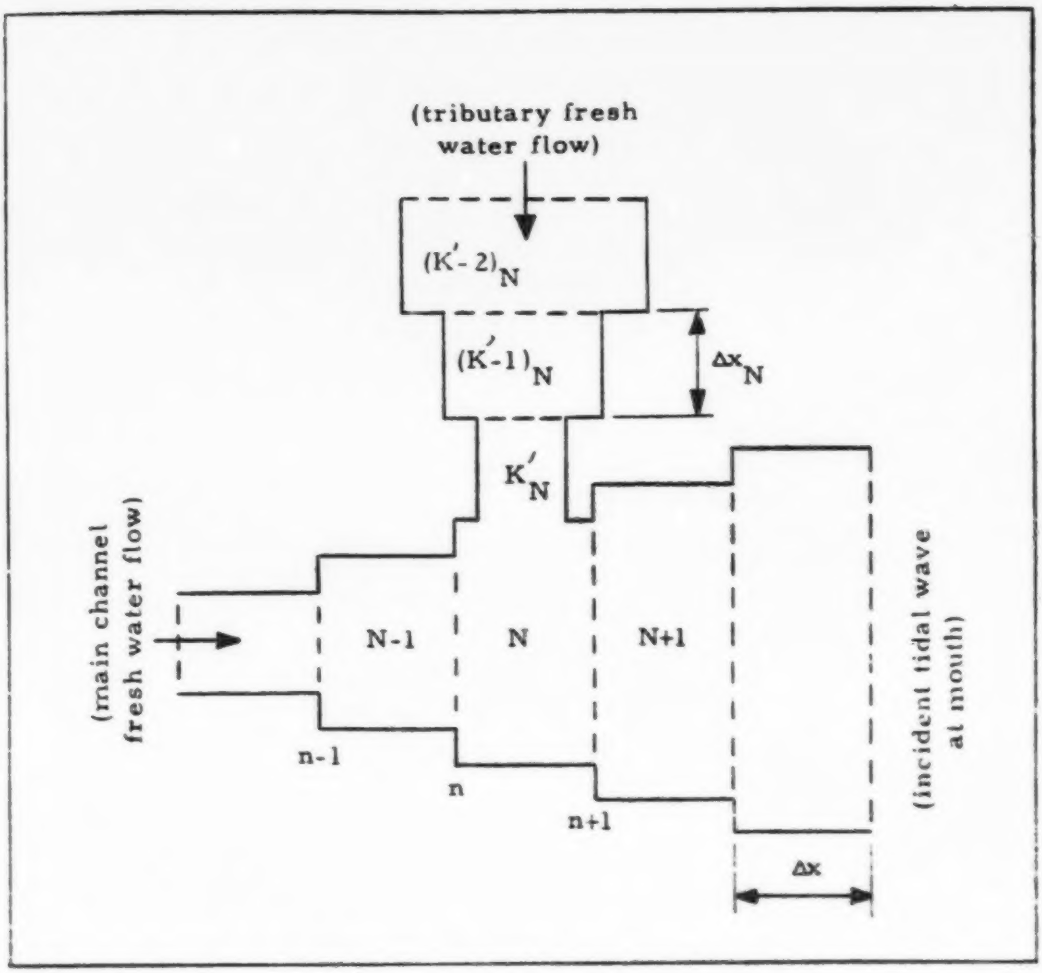
(tributary fresh water flow)
(K'-2)$_N$
(K'-1)$_N$
Δx_N
K'_N
(main channel fresh water flow)
N-1
N
N+1
(incident tidal wave at mouth)
n-1
n
n+1
Δx

FIG. A1 - REPRESENTATION OF ESTUARY CHANNEL AND TRIBUTARY.

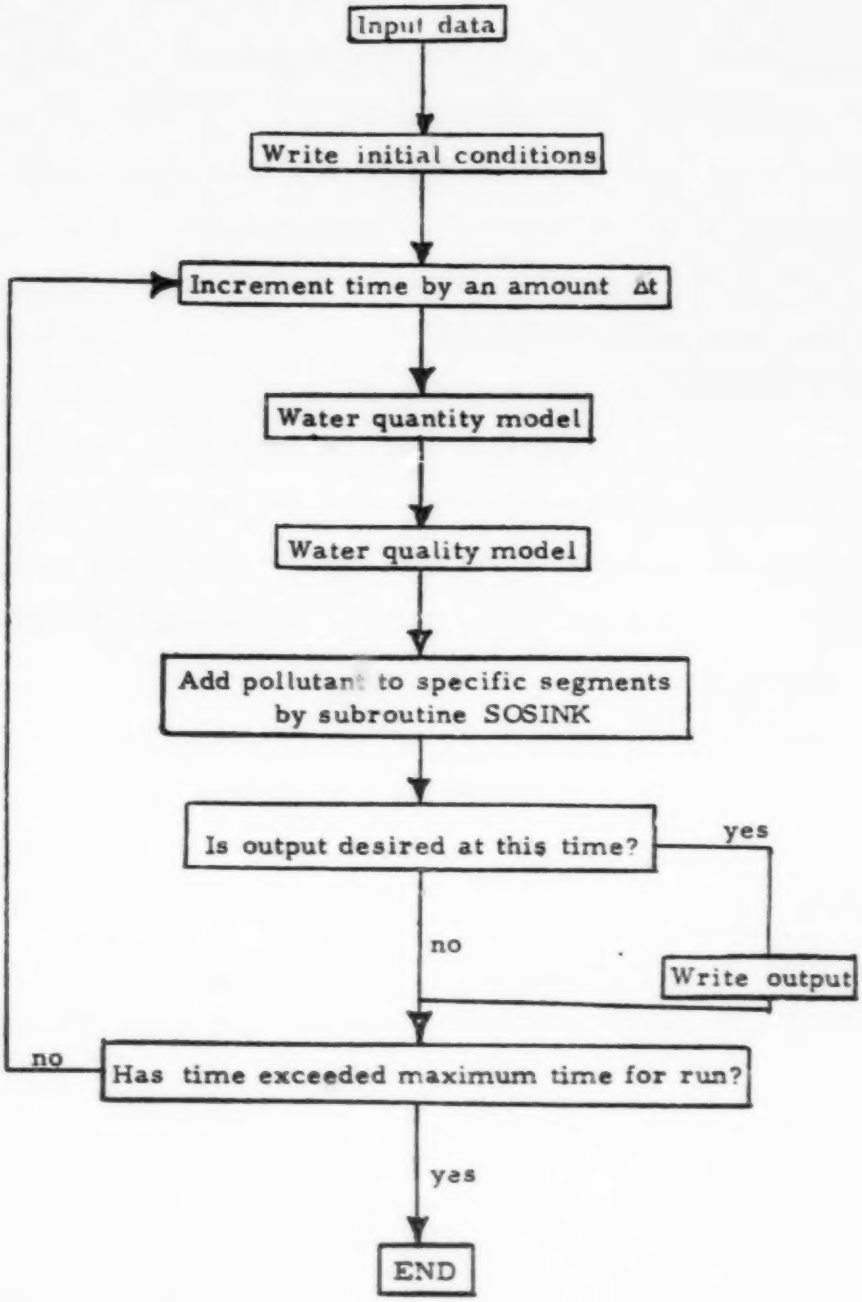
Input data
Write initial conditions
Increment time by an amount Δt
Water quantity model
Water quality model
Add pollutant to specific segments by subroutine SOSINK
Is output desired at this time?
yes
no
Write output
no
Has time exceeded maximum time for run?
yes
END

FIG. A2 - FLOW CHART FOR THE MAIN COMPUTER PROGRAM.

For each time increment, the program begins at the fresh water end of the main channel (segment number one) and calculates flows in each successive segment by means of the water quality model. As the calculations proceed down the estuary, each segment is checked for an intersecting tributary. When tributaries are encountered, control is shifted to a subroutine which calculates tributary inflow. The main channel flow is adjusted by the amount of the tributary flow and the program proceeds to the next segme

After flows have been calculated in all segments, the program returns to segment one and again proceeds down the main channel calculating pollutant concentrations by means of the water quality model. When tributaries are encountered, control is shifted to a sub program which distributes the polluta in the tributary.

When the pollution distribution has been calculated for all segments in the estuary, the program returns to segment number one and proceeds back down the main channel checking for pollution sources. When outfall locations are encountered pollution is injected by subroutine SOSINK.

Results are printed in predesignated times. Output includes the velocity area, dispersion coefficient and concentration in each segment.

WATER QUALITY MODEL

General

Conceptualize a stream as a series of mixed cells of length ΔX as shown in Figure A3. A number of memory locations are established in the computer to record the water quality and quantity conditions within each cell. The longitudinal mixing, as an example, that occurs over a small time interval of length ΔT is simulated by numerically exchanging a given amount of water and thus pollutant in each segment with the two adjacent segments. The amount of such water exchanged between segments is dependent on the length of the time interval, ΔT, the segment size, and the hydraulic conditions being simulated in the stream. The pollutant mass at the end of the time interval is given by the simple mass balance equation

$$\begin{pmatrix}\text{Pollutant Mass}\\ \text{in segment at}\\ \text{time } T+\Delta T\end{pmatrix} = \begin{pmatrix}\text{Pollutant Mass}\\ \text{in segment at}\\ \text{time } T\end{pmatrix} + \begin{pmatrix}\text{Net Mass}\\ \text{exchanged}\\ \text{during } \Delta T\end{pmatrix}$$

This "pollutant exchange", of course, involves the addition and subtraction of the pollutant masses recorded at the appropriate memory locations in the computer. These computations are performed for each segment along the length of the stream and are repeated for successive time intervals in order to describe the change in pollutant mass in each segment (from which the concentration can be calculated) over time due to mixing.

The simultaneous advection and biochemical reactions of a pollutant can also be simulated. Advection is simulated by transferring during each time interval a portion of the pollutant in each segment to the segment immediately downstream. Biochemical reactions are simulated by adding or subtracting appropriate amounts for each segment over each time interval. A pollutant

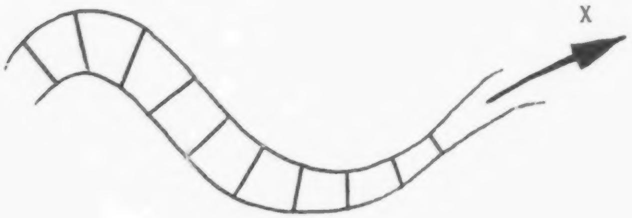

FIG. A3 - STREAM CONCEPTUALIZED AS A SERIES OF MIXED CELLS

outfall can be simulated by adding pollutant mass to the particular segment at the outfall location for each time interval. The simultaneous action of all of these processes is simulated by performing all such exchanges and removals for all segments during each time interval. The process is repeated over a sufficient number of time intervals (of length ΔT) so as to span the time period of interest. If ΔX and ΔT are sufficiently small, the finite-difference results will approximate the continuous processes being simulated.

Each stream segment (Figure A3) will be considered as completely mixed. The concentration within any segment N at time T will be designated by C(N,T). That is C(N,T) is averaged over the space interval, ΔX, but is not averaged over the time interval, ΔT. Concentrations are recorded at the beginning and end of time intervals.

The cross sectional areas are similarly defined. That is, A(N,T) designates the average cross sectional area of segment N at time T.

For the present discussion, only first order biochemical reactions will be considered. The first order reaction coefficient, K_1, may vary with distance and time. The value of K_1 for the entire segment N during the entire time interval beginning at time T will be designated as $K_1(N,T)$.

The mean water velocity, U and the dispersion coefficients, D_L, always appear as products with A, the cross sectional area. For simplicity these products will be designated as UA, the total flow rate, and DA, the total dispersion coefficient. In order to keep the number of subscripted variables to two, the following notation is used. UA(N+1,T) and DA(N+1,T) equal the average values of UA and DA at the interface of segments N and N+1 over a time interval which begins at time T. UA(N,T) and DA(N,T) equal the average values of UA and DA at the interface of segment N and N-1 over a time interval which begins at time, T.

The above finite-difference definitions are not standard definitions. One must closely examine the definitions used in each modeling approach. In the following sections, advection, dispersion, decay and pollutant addition will be individually modeled in finite-difference form. A method of combining these individual processes will then be presented.

Advection

The advection can be conceptualized in finite-difference terms as a water transfer from upstream segments repeated for each time interval, ΔT (see Figure A4). The volume of water transferred in each step is equal to the flow rate between segments times the length of the time interval as shown in Figure A4.

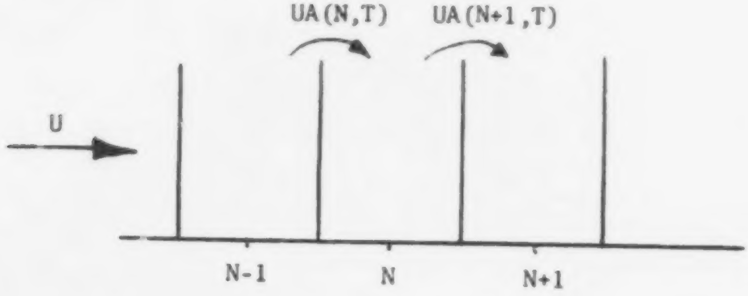

FIG. A4 - FINITE-DIFFERENCE ADVECTION

The mass transferred into segment N will be equal to the volume of water transferred from segment N-1 to segment N (assuming direction of flow from left to right) times the pollutant concentration in segment N-1. That is, the pollutant mass transferred into segment N equals

$$UA(N,T)\Delta TC(N-1,T) \qquad (1)$$

Similarly the pollutant mass transferred out of segment N equals

$$UA(n+1,T)\Delta TC(N,T) \tag{2}$$

The pollutant mass at the start of ΔT will be equal to

$$C(N,T)A(N,T) \tag{3}$$

while the pollutant mass at the end of the time interval will be equal to

$$C(N,T+\Delta T)A(N,T+ \Delta T) \tag{4}$$

Consider a mass balance of pollutant within segment N. One obtains: (mass at end of ΔT) = (mass at start of ΔT) + (mass advected in during ΔT) - (mass advected out during ΔT). Substituting equations (1), (2), (3) and (4) into this mass balance leads to

$$\begin{aligned} C(N,T+\Delta T) = & \frac{C(N,T)A(N,T)}{A(N,T+\Delta T)} \\ & + \frac{UA(N,T)C(N-1,T)\Delta T}{A(N,T+\Delta T)\Delta X} \\ & - \frac{UA(N+1,T)C(N,T)\Delta T}{A(N,T+\Delta T)\Delta X} \end{aligned} \tag{5}$$

Equation (5) is the finite-difference model of advection with variable parameters when the velocity flows from segment N-1 to segment N.

Should the velocity reverse direction, equation (5) must be replaced by equation (6)

$$\begin{aligned} C(N,T+\Delta T) = & \frac{C(N,T)A(N,T)}{A(N,T+\Delta T)} \\ & + \frac{UA(N+1,T)C(N+1,T)\Delta T}{A(n,T+\Delta T)\Delta X} \\ & - \frac{UA(N,T)C(N,T)\Delta T}{A(N,T+\Delta T)\Delta X} \end{aligned} \tag{6}$$

Equation (5) and (6) are subject to the restriction

$$U\Delta T \leq \Delta X \tag{7}$$

Explicit Finite-Difference Model of Dispersion

Consider any stream segment N as illustrated in Figure A5. At time T, the beginning of the time interval, equal elements of water, of volume w(N,T), are exchanged between segments N and N-1. Similarly, equal elements of water, of volume w(N+1,T), are exchanged between segments N and N+1. The elements of water are exchanged and all cells are completely mixed over the time interval ΔT.

The mass of pollutant leaving segment N during this exchange is:

$$w(N,T)C(N,T)+w(N+1,T)C(N,T) \tag{8}$$

while the mass of pollutant entering segment N from segment N-1 and N+1 during ΔT is:

$$w(N,T)C(N-1,T)+w(N+1,T)C(N+1,T) \tag{9}$$

The change in mass in segment n during ΔT equals

$$[C(N,T+\Delta T) - C(N,T)]A(N,T)\Delta X \tag{10}$$

setting the change in mass within segment N equation (10), equal to the mass input to segment n minus the mass output from segment N leads to

$$\begin{aligned} C(N,T+\Delta T) &= C(N,T) \\ &+ \frac{w(N,T)}{A(n,T)\Delta X}\ [C(N-1,T)-C(N,T)] \\ &+ \frac{w(N+1,T)}{A(N,T)\Delta X}\ [C(N+1,T)-C(N,T)] \end{aligned} \tag{11}$$

From a mixing length description the dispersion coefficient may be considered as

$$D_L = qh^1 \tag{12}$$

in which q is the volume rate of water exchanged per unit cross sectional area and h^1 is the effective length of the exchange. From the difference model described above and equation (12), one obtains:

$$D_L = \frac{w\Delta X}{A\Delta T} \qquad (13)$$

and

$$w = \frac{D_L A\Delta T}{\Delta X} \qquad (14)$$

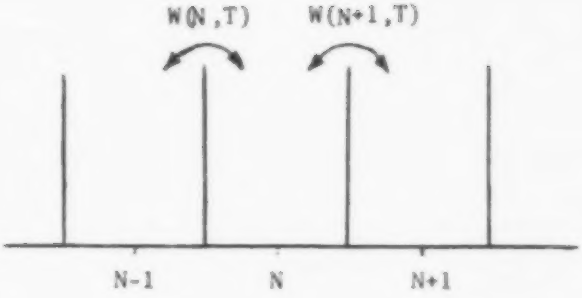

FIG. A5 - FINITE-DIFFERENCE DISPERSION

Using the notation previously given, one obtains

$$w(N,T) = \frac{DA(N,T)\Delta T}{\Delta X} \quad [C(N-1,T)-C(N,T)] \qquad (15)$$

and

$$w(N+1,T) = \frac{DA(N+1,T)\Delta T}{\Delta X} \; [C(N+1,T)-C(N,T)] \qquad (16)$$

Substitution equations (15) and 16) into equation (11) leads to

$$\begin{aligned} C(N,T+\Delta T) &= C(N,T) \\ &+ \frac{DA(N,T)\Delta T}{A(N,T)\Delta X^2} \\ &+ \frac{DA(N+1,T)\Delta T}{A(N,T)\Delta X^2} \end{aligned} \qquad (17)$$

Equation (17) enables one to explicitly obtain the concentration in segment at the end of the time interval. Repeated use of equation (17) will closely simulate the dispersion (and diffusion) process if ΔX and ΔT are sufficientl small.

It is reasonable from the above approach that the total volume of water exchanged during the time interval should not exceed the volume of the segment. That is:

$$w(N,T) + w(N+1,T) \leq A(N,T)\Delta X \qquad (18)$$

Substituting (15) and (16) into (18) leads to

$$\frac{DA(N,T)}{A(N,T)} + \frac{DA(N+1,T)}{A(N,T)} \leq \frac{\Delta X^2}{\Delta T}$$

If D_L and A do not vary with length, X, one obtains from equation (19) the stability requirement for the standard explicit scheme for the approximation of the diffusion equation:

$$\frac{D_L \Delta T}{\Delta X^2} \leq 1/2 \qquad (20)$$

To prevent an oscillation error, one should accept the following requirement.

$$\frac{D_L \Delta T}{\Delta X^2} < 1/2 \qquad (21)$$

First Order Biochemical Reactions

If one assumes that the change of pollutant mass within any segment N that occurs over a time interval of length, ΔT, is proportional to the pollutant mass within the cell during the time interval and proportional to the length of the time interval, one obtains

$$C(N,T+\Delta T) = C(N,T)-K_1(N,T)\Delta T(1-\theta)C(N,T)+\theta C(N,T+\Delta T)] \qquad (22)$$

in which θ is a weighing function ($0 \leq \theta \leq 1$).

The Addition of Pollutants

Pollutants may be added to any stream segment. By equating the pollutant mass in any segment N at the end of the time interval ($T+\Delta T$), to the pollutant mass in the segment at the beginning of the time interval (T) plus the pollutant mass added over the time interval, ΔT, one obtains:

$$C(N,T+\Delta T) = C(N,T) + \frac{m(N,T)\Delta T}{A(N,T)\Delta X} \qquad (23)$$

in which m(N,T) equals the average pollutant mass input rate into segment N over the time interval beginning at time T.

Combining Dispersion, Advection, Decay and Additions

Equations (5), (17), (22) and (23) can be simply combined in order to simulate the simultaneous occurrence of advection, dispersion, decay and additions. One merely utilizes each of these four equations sequentially. The final concentration results of a given step serve as the initial concentrations for the following step. As an example, equation (5) would be used to describe the concentration changes due to advection alone. The results of equation (5) would then be used for the initial conditions for the dispersion equation (17). That is $C(N,T+\Delta T)$ from equation (5) would serve as $C(N,T)$ in equation (17). The results $(T+\Delta T)$ of equation (17) would then serve as initial (T) concentrations for equation (22). The $C(N,T+\Delta T)$ values obtained from equation (22) would serve as the $C(N,T)$ values of equation (23). Change in the cross sectiona area, $A(N,T)$, should be included during the advection step. The use of all four equations would describe the pollutant concentration changes over the time interval due to advection, dispersion, decay and additions. These steps would then be repeated for successive time intervals (of length, ΔT) until the computations covered the desired time span being simulated. The computational sequence of equations (5), (17), (22) and (23) can be changed in any order with no significant change in the results.

Equations (5) and (6) produce a numerical mixing error. This error can be described by an effective or pseudo dispersion coefficient given by

$$D_p = \frac{U}{2}\left[\Delta X - U\Delta T\right] \qquad (24)$$

In order to compensate for this error, D_p from equation (24) must be subtracted from the actual dispersion coefficient used in equation (17) for each time and length interval.

WATER QUANTITY MODEL

The most simple method for estimating stream velocities is to assume uniform flow throughout the estuary and apply a sinusoidal velocity at the mouth. A more realistic method is to determine water surface elevations as a function of distance and time and calculate flows from known characteristics of the channel. This can be accomplished by solving the continuity and momentum equation for unsteady flow. Although this method is accurate, a great amount of computer time is required. A more efficient method has been to use changes in water surface elevations to calculate average flows over small time intervals, i.e., (average flow out of segment) = (average flow in) - (change in volume) (Fisher, 1969). This method has been adopted for the present study and can be represented in finite-difference terms as follows for flow in the direction shown in Figure A1.

$$UA(N,T) = UA(N-1,T) + [A(N,T-1) - A(N,T)] \frac{\Delta X}{\Delta T} \qquad (25)$$

By using this approach, the problem is reduced to one of finding an efficient means for predicting water surface elevations (H).

Fisher (1969), in studies of Bolinas Lagoon, California, used observed values of H over a few tidal cycles. The use of tabulated values becomes awkward for long period of analysis. Dorlhelm and Wollhiser (1968) predict H by propagating a sine shaped tidal wave up the estuary. Tidal actions in most real estuaries do not conform to this simple representation however.

Frequently a reflected sine wave can be used to predict tidal heights along an estuary (Ippen, 1966). Consider the channel profile of length L shown in Figure A6. An imposed wave is assumed to travel up the estuary from the mouth. A hypothetical boundary exists at the end of the estuary which reflects a portion of the incident wave. The water surface at a point x feet from the

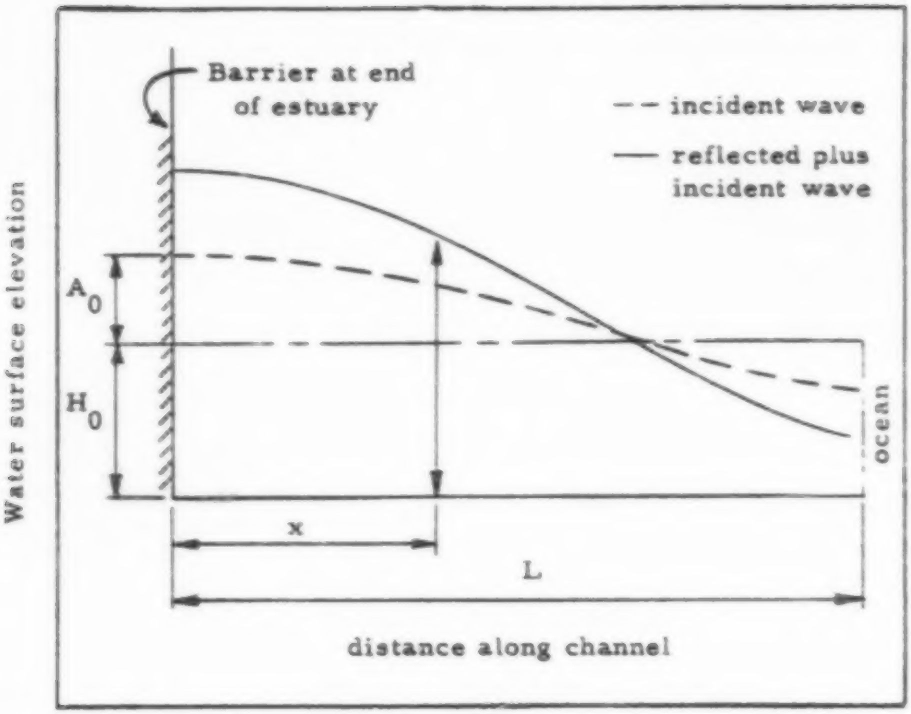
Barrier at end of estuary
-- incident wave
— reflected plus incident wave
Water surface elevation
A_0
H_0
ocean
x
L
distance along channel

FIG. A6 - REFLECTED TIDAL WAVE.

boundary can be predicted by superimposing the height of the reflected wave onto the incident wave. The effects of friction can be approximated by assuming an exponential reduction in wave height with distance. Mathematically, the tidal height can be represented as (Glenne, 1969):

$$H = H_0 + a[e^{\mu x}\cos(\delta T + kx) + \beta e^{-\mu x}\cos(\delta T - kx)] \qquad (26)$$

where H_0 = average water surface elevation, a = amplitude of incident wave, μ = constant representing channel friction, δ = wave frequency, k = portion of a tidal cycle required for the wave to travel one unit of estuary length, and β = fraction of wave reflected. For short tributaries the water surface elevation can be assumed equal to that in the main channel at the point of intersection. For long tributaries, program control is shifted to a subprogram which propagates the wave up the tributary channel in accordance with equation (26) where a = amplitude of incident wave at the mouth of the tributary.

The solution of equation (26) for every channel and tributary segment during each time increment would be very time consuming. Therefore a method of approximating equation (26) was adopted. Figure A7 shows the flow chart for the subprogram used to calculate water surface elevations and cross section areas. The incident wave at the mouth of the estuary is represented for one and a quarter tidal periods by a series of chords as shown in Figure A8. This method of describing the wave allows complete freedom for selecting any shape wave at the mouth of the estuary, i.e., it is not limited to a cosine function. The amount of error introduced by representing a smooth curve with a series of chords is a function of the number of increments into which the tidal cycle is divided. The error in representing a cosine curve by this method is shown in Figure A9 where i is the maximum difference between any chord and the true curve based on an amplitude of one.

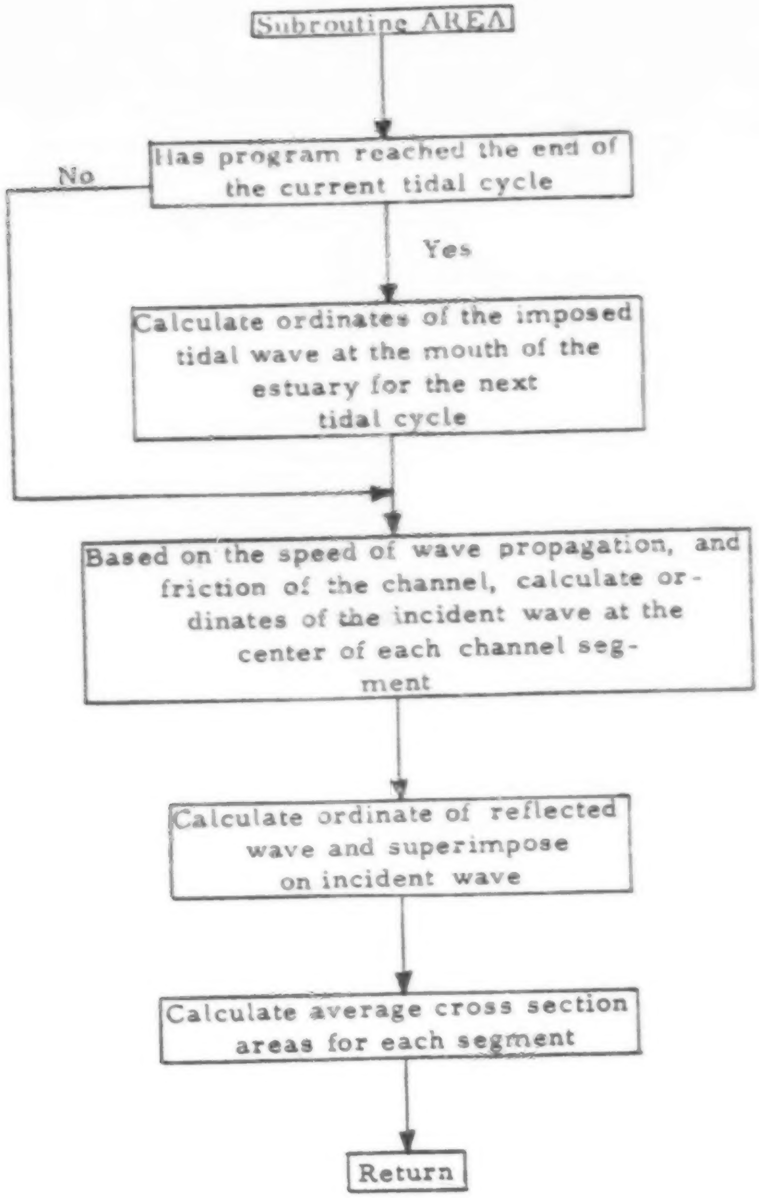
Subroutine AREA
Has program reached the end of the current tidal cycle
No
Yes
Calculate ordinates of the imposed tidal wave at the mouth of the estuary for the next tidal cycle
Based on the speed of wave propagation, and friction of the channel, calculate ordinates of the incident wave at the center of each channel segment
Calculate ordinate of reflected wave and superimpose on incident wave
Calculate average cross section areas for each segment
Return

FIG. A7 - FLOW CHART FOR SUBROUTINE "AREA".

For any particular time at the mouth of the estuary, T, the ordinate of the imposed wave at any point, x, in the estuary can be calculated by determinining the time required for the wave to move up the channel to that point. This is the lag time and is represented by TRAV on Figure A8. For this study, the time lag was expressed as:

$$\text{TRAV} = c(1-x)$$

where c is wave celerity, x is the distance from the fresh water end, and L is the length of the estuary. More accuracy could possibly be achieved by allowing c to vary as a function of depth; however, at the sacrifice of computer time. Once T_x is located (Figure A8), the elevation is obtained by interpolating between points M and M + 1.

The ordinate of the reflected wave is obtained in a similar manner. A portion of the incident wave is assumed to bounce off the boundary at the end of the estuary and travel back towards the mouth at the same celerity. The total lag time for the wave to travel from the mouth back to point x can be calculated by:

$$\text{TRAV} = c(L+x)$$

Friction is incorporated in the model by reducing the ordinates by an exponential function of the distance traveled by the wave, i.e., $e^{-\mu(L-x)}$ for the incident wave and $e^{-\mu(L+x)}$ for the reflected wave. The water surface elevation is then obtained by superimposing the ordinates of the incident and reflected waves. Friction need not be represented by an exponential function; however, it was selected so that existing methods (Ippen, 1966) could be used to estimate the parameters μ and k. It may not be the most realistic representation, however, because the major frictional influence is exerted near the mouth of the estuary and the frictional effect decreases with distance up

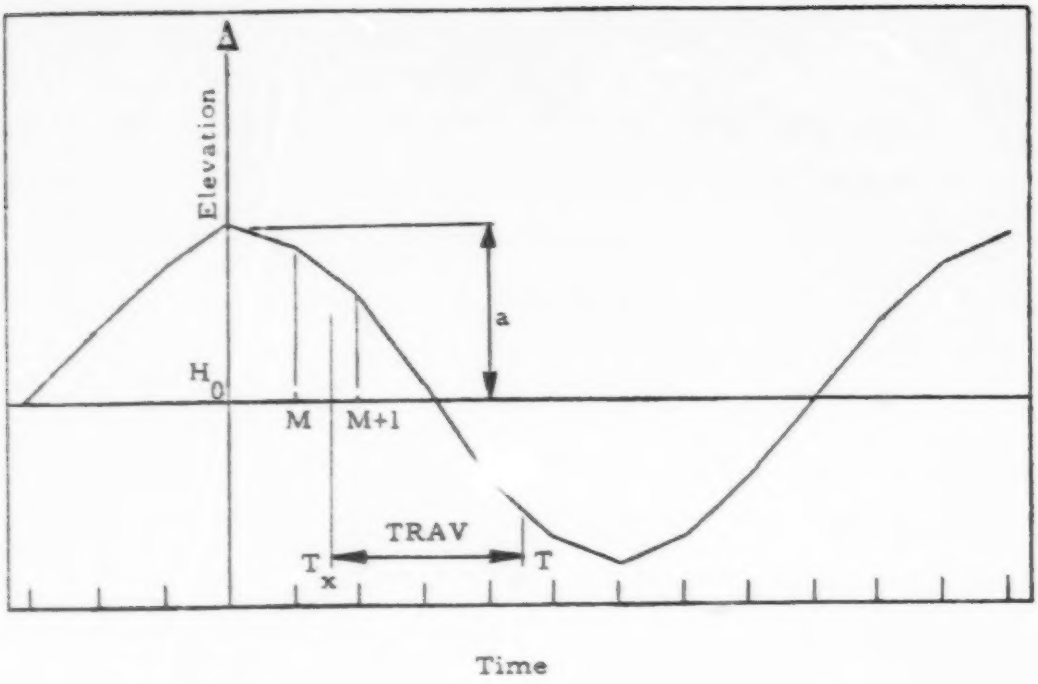
Elevation
H_0
M
M+1
a
TRAV
T_x
T
Time

FIG. A8 - TIDAL WAVE REPRESENTATION AT THE MOUTH OF AN ESTUARY

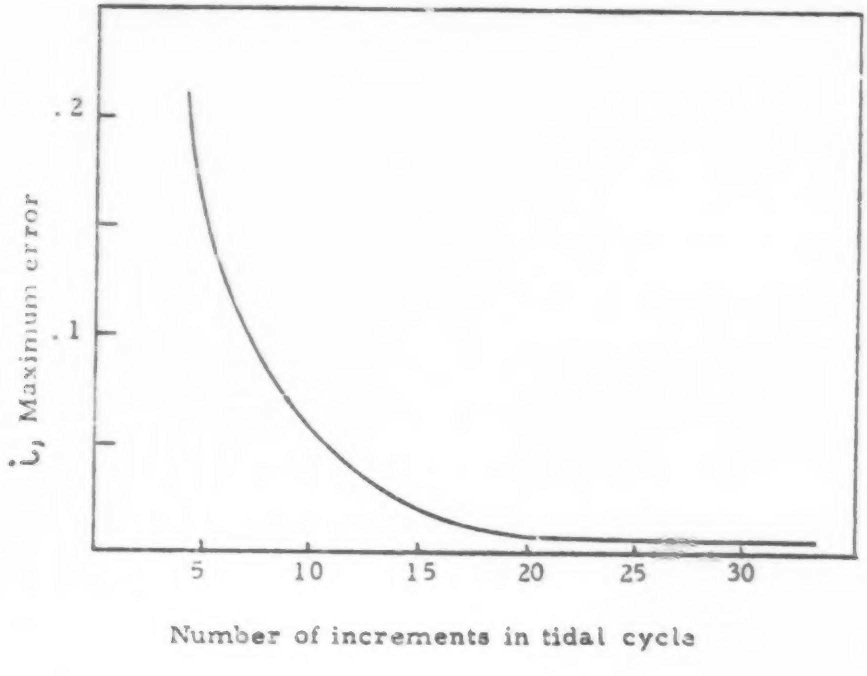

FIG. A9 - ERROR INTRODUCED BY LINEAR INTERPOLATION

the estuary. Conversely, in some real estuaries the effect of friction would probably be least near the mouth and increase with distance up the estuary.

Cross section areas are calculated as a function of the water surface elevation and side slopes of the channel at each segment.

In order to calculate flows by means of equation (25) it is necessary to know the flow across the interface of segment one at the upper end of the estuary and in every tributary. For a completely reflected wave all of the tidal induced flow is reflected and, therefore, the flow across the first interface is equal to the fresh water inflow. Physically this can be visualized as a waterfall forming a complete barrier at the end of the estuary. However, when the upstream boundary reflects only a fraction, β, of the incident wave amplitude, a certain amount of flow will be induced at segment one due to tidal action beyond the boundary. When this flow is neglected, significant errors may be introduced for values of β less than one.

The tidal induced flows at the boundary can be calculated by extending the hydraulic model beyond the boundary a distance necessary for the unreflected portion of the wave to become significantly attenuated by friction. For progressive waves with low friction this method may require excessive computer time. One approach to reduce computer time and still approximate flows across the first interface would be to increase the friction coefficient beyond the boundary. Errors introduced by this approximation would have to be investigated for each individual case.

If the reflected wave is not completely attenuated when it reaches the mouth of the estuary, the calculated water surface elevation will not coincide with the incident wave and a discontinuity will occur at the ocean boundary. Ippen (1966) avoids the problem by applying the incident wave at the end of the estuary instead of the mouth. However, tidal fluctuations are generally not recorded at the upper end of an estuary, and this approach is not always practical.

If there is sufficient friction in the channel, or if β is low, the discontinuity will be negligible. When a substantial discontinuity does exist at the ocean boundary, a driving wave must be found such that superposition of the reflected wave will result in water surface elevations which agree with observed data. Finding a driving wave is difficult, but it can be done by trial and error for short runs.

The water quantity model was computed for one tidal cycle by adjusting the model to fit measured results (Grenney and Bella, 1972). The single tidal cycle was repeated to simulate longer runs with a minimum computer time.

A description of program subroutines is given in Table A1 and a listing of the programs is provided in Table A2.

TABLE A1 - DESCRIPTIONS OF COMPUTER PROGRAMS

PROGRAM ESTREF: main program
  a) Controls input/output and subroutines
  b) Calculates initial conditions
  c) For each ΔX and ΔT calculates: average flows, convection, dispersion, and decay

SUBROUTINE INPUT: reads input coefficients and identification number scheme for finite-difference representation of estuary.

SUBROUTINE INCON: reads initial conditions values for variables; calculates cross-sectional areas and stream surface widths for mean water depth; and sets up initial concentrations in each segment.

SUBROUTINE INAREA: calculates initial cross-sectional areas at each segment given an initial tidal height at the mouth.

SUBROUTINE TIDE: calculates tidal height at the mouth as a function of time.

SUBROUTINE AREA: propagates tidal wave inland and calculates cross-sectional areas at each segment for each ΔT.

SUBROUTINE SOSI: provides input or removal of material at specified segments and times to represent exogenous sources and sinks.

FUNCTION FLWU: fresh water flow entering the system at the inland boundary.

TABLE A2---LISTING OF COMPUTER PROGRAMS FOR ESTUARY MODEL

```
      PROGRAM FSTHEF
      COMMON A0(300),B0(300),S0(300),TPAV(300),D(300),ID(300),EXP(300),
     1EXPH(300),DHK(300),UH(300),A(300,2),C1(300),AA2(300),NTOT,ELM,
     2U,THA,DTM,T,THAX,CK1,QU(50),LL,C11,C1N,REPT,DTH,MTOT,MO,TO,TE,
     3ADTH,ALFA,LAST,DX,EL, UA2, JJJ,TRAVH(300),KKC
      DIMENSION UA(300),C2(300),DPA(300),UAA(300)
   40 CALL INPUT
      TREPT=REPT
      THA1=1.0-THA
      DTH=DTM/60.0
      DT=DTM*60.0
      EL=ELM*5280
      CK1=CK1/86400
      RNTOT=NTOT
      DX=EL/RNTOT
      DTX=DT/DX
      KIP=0
      F3=(1-CK1*DT*THA1)/(1+CK1*DT*THA)
      J=1
      K=2
      KOU=1
      J11=1
      LASTP1=LAST+1
C             INITIAL CONDITIONS
      CALL INCON
      CALL INAREA
      UA(2)=FLWU(T)
      C1(1)=C11
      C1(LAST+1)=C1N
      WRITE(2,50) NTOT,ELM,DX,DTM,U,THA,CK1,LL
   50 FORMAT(1H ,/ / / / 1H ,3X,I5, 3F12.3 //1H ,3X,3F12.3,I5 //)
      WRITE(2,54) T
   54 FORMAT(1H ,/ 1H ,3X,F12.2)
      ICON1=1
      ICON2=LAST+1
      WRITE(2,55) (I,A(I,J),C1(I),EXP(I),EXPH(I),I=1,LASTP1)
   55 FORMAT(1H ,4X,I4,F15.2,F15.4,2F10.4)
   35 T=T+DTH
      CALL AREA(K)
C                 AVE FLOWS AT ALL SECTIONS
      DO 8 N=2,LAST
      NP=N+1
      UA(2)=FLWU(T)
      UA(NP)=UA(N)+(A(N,J)-A(N,K))/DTX
      VELUC=2.*UA(N)/(A(N,K)+A(N,J))
      D(N)=50.0*ABS(VELUC)
    8 CONTINUE
      L=1
      DO 72 N=2,LAST
      IF(N-ID(L)) 72,71,72
   71 CALL SOSI(T,RATE)
      C1(N)=C1(N)+RATE*DTH/(A(N,J)+A(N,K))/2.0
      L=L+1
   72 CONTINUE
C                   CONVECTION AT ALL SECTIONS
      IF(UA(2)) 61,60,60
   61 F1=UA(2)*C1(2)
      DPA(2)=-UA(2)*(DX+UA(2)*DT/A(2,K))/2.0
      GO TO 62
   60 F1=UA(2)*C1(1)
      DPA(2)= UA(2)*(DX-UA(2)*DT/A(2,K))/2.0
```

TABLE A2 (continued)---LISTING OF COMPUTER PROGRAMS FOR ESTUARY MODEL

```
   62 DAA(2)=D(2)*AA2(2)-DPA(2)
      DO 63 N=2,LAST
      NP=N+1
      IF(UA(NP)) 64,65,65
   64 F2=UA(NP)*C1(NP)
      DPA(NP)=-UA(NP)*(DX+UA(NP)*DT/A(NP,K))/2.0
      GO TO 66
   65 F2=UA(NP)*C1(N)
      DPA(NP)= UA(NP)*(DX-UA(NP)*DT/A(NP,K))/2.0
   66 C2(N)=(C1(N)*A(N,J)+(F1-F2)*DTX)/A(N,K)
      DAA(NP)=D(NP)*AA2(NP)-DPA(NP)
      F1=F2
   63 CONTINUE
C             DISPERSION AT ALL SECTIONS
      F4=((C2(1)-C2(2))*DAA(2))*(1.0-ALFA)
      DO 9 N=2,LAST
      F5=(C2(N+1)-C2(N))*DAA(N+1)
      C2(N)=C2(N)+(F5+F4)*DTX/(DX*A(N,J))
      F4=-F5
    9 CONTINUE
C              DECAY AT ALL SECTIONS
      DO 11 N=2,LAST
      C1(N)=C2(N)*F3
   11 CONTINUE
C                        OUTPUT
      IF(QU(KOU)-T) 25, 25,24
   25 KOU=KOU+1
      WRITE(2,52) T
   52 FORMAT(1H ,/ 1H ,3X, F12.5)
      WRITE(2,56) ICON1,DH(1),C1(1)
   56 FORMAT(1H ,I5,F12.4,26X,F15.4)
      DO 21 I=2,LASTP1
      VELOC=2.*Q(I)/(A(I,K)+A(I,J))
      WRITE(2,53) I,DH(I),VELOC,A(I,K),C1(I)
   53 FORMAT(1H ,I5,F12.4,F14.4,F12.1,F15.4)
   21 CONTINUE
   24 IDUM=J
      J=K
      K=IDUM
      IF(T-TMAX) 35,32,32
   32 IF(I-IREPT) 41,40,41
   41 CALL EXIT
      END
      SUBROUTINE INPUT
      COMMON A0(300),B0(300),S0(300),TRAV(300),D(300),ID(300),EXP(300),
     1EXPH(300),DHK(500),QH(300),A(300,2),C1(300),AA2(300),NTUT,ELM,
     2U,THA,DTM,T,TMAX,CK1,QU(50),LI ,C11,CIN,NEPI,DTH,NTOT,MO,TO,TE,
     3ADTH,ALFA,LAST,DX,EL, UA2, JJJ,TRAVH(300),KKC
      NTOT=FFIN(1)
      ELM=FFIN(1)
      THA=FFIN(1)
      DTM=FFIN(1)
      T=FFIN(1)
      TMAX=FFIN(1)
      CK1=FFIN(1)
      NTIME=FFIN(1)
      DO 4 I=1,NTIME
      QU(I)=FFIN(1)
    4 CONTINUE
      JJJ=FFIN(1)
      LL=FFIN(1)
```

TABLE A2 (continued)---LISTING OF COMPUTER PROGRAMS FOR ESTUARY MODEL

```
      DO 3 I=1,LL
      ID(I)=FFIN(1)
    3 CONTINUE
      ID(I+1)=0
      REPT=FFIN(1)
      LAST=NTOT+1
      RETURN
      END
      SUBROUTINE INCON
      COMMON AO(300),BO(300),SO(300),TRAV(300),D(300),ID(300),EXP(300),
     1EXPR(300),DHK(500),UM(300),A(300,2),C1(300),AA2(300),NTOT,ELM,
     2U,THA,DTM,T,TMAX,CK1,DU(50),LL,C11,CIN,REPT,DTM,NTOT,MO,TO,TE,
     3ADTH,ALFA,LAST,DX,EL, UA2, JJJ,TRAVR(300),RKC
      RKC=FFIN(1)
      U=FFIN(1)
      ALFA=FFIN(1)
      AAA=FFIN(1)
      BBB=FFIN(1)
      SSS=FFIN(1)
      TTT=FFIN(1)
      DDD=FFIN(1)
      CCC=FFIN(1)
      C11=FFIN(1)
      UA2=FFIN(1)
      CIN=FFIN(1)
      LSTP1=LAST+1
      AO=1000.
      Y=DX/5280.
      DO 1 I=1,LSTP1
      AO(I+1)=382.5*Y-160
      IF(AO(I+1)-1000.) 10,10,11
   10 AO(I+1)=1000.
   11 YADJ=Y-3.875
      BO(I+1)=(-5.0476)*YADJ*YADJ+50.0476*YADJ+127.0
      IF(BO(I+1)-135.0) 12,12,13
   12 BO(I+1)=135.0
   13 CONTINUE
      SO(I)=SSS
      TRAV(I)=TTT
      D(I)=DDD
      C1(I)=CCC
      Y=Y+DX/5280.0
    1 CONTINUE
      RETURN
      END
      SUBROUTINE INAREA
      COMMON AO(300),BO(300),SO(300),TRAV(300),D(300),ID(300),EXP(300),
     1EXPR(300),DHK(500),UM(300),A(300,2),C1(300),AA2(300),NTOT,ELM,
     2U,THA,DTM,T,TMAX,CK1,DU(50),LL,C11,CIN,REPT,DTM,NTOT,MO,TO,TE,
     3ADTH,ALFA,LAST,DX,EL, UA2, JJJ,TRAVR(300),RKC
      CALL TIDE
      J=1
      LASTP1=LAST+1
      U=U/5280.
      TRAV(1)=RKC*EL/(ADTH*3600.)
      EXP(1)=2.71828**(-U*EL)
      TRAVR(1)=TRAV(1)
      EXPR(1)=EXP(1)
      EXP(LASTP1)=1.0
      TRAV(LASTP1)=TRAVR(LASTP1)=EXPR(LASTP1)=0.0
      Y=DX/2.0
```

TABLE A2 (continued)---LISTING OF COMPUTER PROGRAMS FOR ESTUARY MODEI

```
      TRAVX=(T-TO)/ADTH+HO
      IN=LAST
      DO 4 N=2,LAST
      Z=EL+EL-Y
      EXP(IN)=2./1828**(-U*Y)
      EXPR(IN)=ALFA*(2.71828**(-U*Z))
      TRAV(IN)=HKC*Y/(ADTH*3600.)
      TRAVR(IN)=HKC*Z/(ADTH*3600.)
      Y=Y+DX
      IN=IN-1
    4 CONTINUE
      DO 5 IN=1,LASTP1
      TINC=TRAVX-TRAV(IN)
      M=TINC
      RINC=M
      DH(IN)=EXP(IN)*(DHK(M)+(DHK(M+1)-DHK(M))*(TINC-RINC))
      TINC=TRAVX-TRAVR(IN)
      M=TINC
      RINC=M
      DHR=EXPR(IN)*(DHK(M)+(DHK(M+1)-DHK(M))*(TINC-RINC))
      DH(IN)=DH(IN)+DHR
      A(IN,J)=AO(IN)+DH(IN)*(BO(IN)+DH(IN)*SO(IN))
    5 CONTINUE
      RETURN
      END
      SUBROUTINE AREA(K)
      COMMON AO(300),BO(300),SO(300),TRAV(300),D(300),IO(300),EXP(300),
     1EXPR(300),DHK(500),DH(300),A(300,2),C1(300),AA2(300),NTOT,ELM,
     2U,THA,DTM,T,TMAX,CK1,DJ(50),LL,C11,CIN,REPT,DTH,HTOT,HO,TO,TE,
     3ADTH,ALFA,LAST,DX,EL, UA2, JJJ,TRAVR(300),HKC
      IF(T-TE) 1,2,2
    2 TO=TE
      TE=TO+(HTOT-HO)*ADTH
    1 TRAVX=(T-TO)/ADTH+HO
      LASTP1=LAST+1
      TINC=TRAVX-TRAV(1)
      M=TINC
      RINC=M
      DH(1)=(DHK(M)+(DHK(M+1)-DHK(M))*(TINC-RINC))*EXP(1)
      TINC=TRAVX-TRAVR(1)
      M=TINC
      RINC=M
      DHR=EXPR(1    )*(DHK(M)+(DHK(M+1)-DHK(M))*(TINC-RINC))
      DH(1)=DH(1)+DHR
      A(1,K)=AO(1)+DH(1)*(BO(1)+DH(1)*SO(1))
      DO 6 IN=2,LASTP1
      TINC=TRAVX-TRAV(IN)
      M=TINC
      RINC=M
      DH(IN)=EXP(IN)*(DHK(M)+(DHK(M+1)-DHK(M))*(TINC-RINC))
      TINC=TRAVX-TRAVR(IN)
      M=TINC
      RINC=M
      DHR=EXPR(IN)*(DHK(M)+(DHK(M+1)-DHK(M))*(TINC-RINC))
      DH(IN)=DH(IN)+DHR
      A(IN,K)=AO(IN)+DH(IN)*(BO(IN)+DH(IN)*SO(IN))
      AA2(IN   )=(A(IN-1,K)+A(IN,K))/2.0
    6 CONTINUE
      AA2(2)=A(1,K)
      RETURN
      END
```

TABLE A2 (continued)---LISTING OF COMPUTER PROGRAMS FOR ESTUARY MODEL

```
      SUBROUTINE TIDE
      COMMON AO(300),BO(300),SO(300),TRAV(300),D(300),IU(300),EXP(300),
     1EXPR(300),DHK(500),UH(300),A(300,2),C1(300),AA2(300),NTOT,ELM,
     2U,THA,DTM,T,TMAX,CK1,DU(50),LL,C11,C1N,REPT,DTH,NTOT,NO,TO,TE,
     3ADTH,ALFA,LAST,DX,EL, UA2, JJJ,TRAVR(300),RKC
      TO=T
      PER=12.3333
      HEIGHT=1.39
      TE=T+PER
      ADTH=PER/32.0
      NTOT=50
      NO=18
      TX=TO-17.0*ADTH
      DO 1 I=1,NTOT
      DHK(I)=HEIGHT*COS(6.2831853*TX/PER)
      TX=TX+ADTH
    1 CONTINUE
      RETURN
      END
      FUNCTION FLOW(T)
      FLOW=950.0
      RETURN
      END
      SUBROUTINE SOST(T,RATE)
      IF(4.9-T) 1,2,2
    1 RATE=4.5E3
      GO TO 3
    2 RATE=0.0
    3 RETURN
      END
 CARD COUNT      274
```